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Porous materials
for a green future

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ORAL ABSTRACTS

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1014 - INTERACTIONS OF BACTERIA AND ZEOLITES

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Zeolites have different interactions with bacteria, depending on the type of zeolitic material (natural zeolitized tuffs (NZ), modified NZ or synthetic zeolites) and bacterial species to be affected (e.g. useful or pathogenic bacteria). In this work, the review of bacteria-zeolites interactions is given. As a model useful bacterium Acinetobacter junii, which is used in the tertiary-stage wastewater treatment, is chosen. An emerging hospital pathogen Acinetobacter baumannii is chosen as a model pathogenic bacterium. Clinoptilolite rich NZ is a promising material for the immobilization of bacteria in both nutrient-poor and nutrient-rich water. Both A. junii and A. baumannii, with hydrophilic or hydrophobic cell surface, could be immobilized onto NZ in the form of biofilm within 24h of contact. The extent of bacterial immobilization increases with the decrease of particle size of NZ. The extent of bacterial immobilization on single NZ cannot be predicted by mineralogical and chemical analysis of NZ, its cation exchange capacity or zeta potential [1].

The NZ modified with Cu(II) or benzalkonium cations act bactericidal against A. baumannii within 1h of contact. The Ni(II) or Zn(II) modified NZ act slightly antibacterial [2]. The surfactant-modified NZ with monolayer, partial bilayer or bilayer hexadecyltrimethylammonium coverage have the bactericidal effect. In the case of partial monolayer hexadecyltrimethylammonium coverage bacteria are not affected [3]. The addition of 1 wt% of Cu(II) modified NZ shortens the survival of A. baumannii in soils. The addition of 0.1 wt% of Ag(I) modified NZ to slightly acidic or alkaline soil completely removes viable A. baumannii within 1 h of contact, with negligible impact on native soil bacteria [4].

Commercial synthetic zeolites of Linde Type A (LTA) in water show the antibacterial effect in the concentration range 0.1-1 wt%. The mechanism of LTA toxicity is explained by the hydrolysis of LTA in water and leaching of aluminosilicate species that destroy bacterial cells [5].

Zeolites can find wide applications regarding bacteria. Clinoptilolite rich NZ are excellent carriers of useful bacteria, like those in wastewater treatment process (range of 109 bacteria per one gram). The NZ modified with Ag(I), Cu(II) or cationic surfactant act antibacterial and can be applied in disinfection of water and remediation of soils contaminated with human pathogens. The antibacterial effect compatible to the modified NZ can be achieved by synthetic zeolite LTA.

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1018 - CHANNELS VS. CAGES HOW CAVITIES GEOMETRY GOVERN THE PRESSURE MEDIATED CRYSTAL FLUID INTERACTION

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The compressional path and the structural evolution of microporous materials compressed in a pressure-transmitting fluid are substantially affected by the potential crystal–fluid interaction, governed by the penetration of new molecules through the zeolitic cavities in response to applied hydrostatic pressure [1–3]. This phenomenon, which can take place at kilobar pressure and promote a relevant mass transfer from fluids to structurally-incorporated molecules, opened new scenarios in industrial processes (i.e., tailoring new materials as catalysts) and even in natural sciences (i.e., to better understand the role of natural zeolites as carrier of molecules in geological environments at high pressure and temperature). The experimental findings reported so far showed that not all the zeolites react with a pressure-mediated intrusion of new monoatomic species or molecules from the pressure-transmitting fluids [4]. A series of variables have been observed to govern the pressure-mediated sorption phenomena and, among those, the most relevant are: the "free diameters" of the cavities, the chemical nature and the bonding configuration of the extra-framework population, the partial pressure of the penetrating molecule in the fluid (if the fluid is a mix of penetrating and non-penetrating molecules), the rate of P-increase, the surface/volume ratio of the crystallites under investigations, and the temperature at which the experiment is conducted. For example, zeolites with well-stuffed channels (e.g., natural zeolites) tend to hinder the penetration of extra molecules from the fluids through the cavities, when compressed at room temperature [3,4].

In this presentation, an overview of the pressure-mediated intrusion phenomena is provided, based on the previous experimental findings and computational modelling studies [3,5], with a comparative analysis about the role played by cavities geometry: can channels and cages govern differently the sorption phenomena at high pressure?

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1239 - ARE ZEOLITES STILL KEY PLAYERS FOR THE XXITH CENTURY ENERGY ROADMAP

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Abstract

“Super big-two” zeolites, having either the FAU or MFI topology, are by far the most important active catalysts used in refineries, as for instance in the fluid catalytic cracking (FCC) process for converting gasoil into valuable products [1]. It is not exaggerating to state that not a single drop of gasoline has been produced by a means other than the FCC process.
Unfortunately, with growing fossil fuel utilization and industrial activities, along with World population increase above 7 billions in 2022, the amount of greenhouse CO2 emission is continuously rising, leading to severe climate change issues [2]. A new paradigm needs therefore to be set with the emergence of alternative energy resources.

In the energy context of the XXth century, after decades of significant optimization of zeolite synthesis, along with more sophisticated characterization tools, those amazing microporous materials became the leaders for performing acid-catalyzed reactions.

The question now arise, will this still be the case for the new energy roadmap of the XXIth century? In the extended presentation, we will try to answer this question while selecting few issues that one will face and hopefully solve: CO2 capture and utilization, methanol economy [3], H2 production, or biofuels.

Extended Abstract

Chemistry relies on the design and control of systems over multiple-length scales ranging from the molecule to the crystal [4]. The assembly at the molecular level involves at least two species, based on non-covalent interactions (hydrogen bonding, electrostatic forces, van der Waals forces, metal-ion coordination), being the cornerstone of long-range organization [5]. Though covalent bonding prevails in zeolites, the latter are meta-stable materials, being produced after successive meta-stable steps [6]. The rational design of zeolites for a targeted reaction frequently remains a challenge that limits its industrial production and application. In this regard, zeolites synthetized via two independent strategies were investigated: (i) the ‘fluoride route’ revisited giving rise to (almost) perfect giant crystals [7]; (ii) the use of biomass residues to guide the zeolite nanocrystals self-assembly [8].
Both types of catalysts have demonstrated good to outstanding performances and selectivities in the reaction of methanol-to-hydrocarbons, either producing light olefins (MTO) or gasoline fraction (MTG). The effect of different synthesis parameters modification on zeolite crystallinity, acid site density, extra-framework aluminum spcies, crystal size and morphology has been investigated ‘in-depth’ and correlated with the data acquired from acid catalysed reactions. Though those results appear promising, one still has to bridge the gap between the potential at lab-scale and future industrial implementation, while overcoming issues related to shaping, mass transfer, process safety, economics and even geopolitics.

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1244 - ZEOLITE NANOSHEETS IN SOLUTION PRECURSORS OF 'UNFEASIBLE' NANOSCALE MATERIALS

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Chemical and related industries such as petroleum processing and pharmaceuticals provide many products that are used in everyday life and are necessary to maintain the modern way of life. These industries are heavily dependent on catalysis for efficient production. Zeolites are one of the most efficient and extraordinary catalysts having 3-dimensional (3D) aluminosilicate networks which can also form 2-dimensional (2D) structures, composed of ultrathin layers with thickness not greater than a few nanometers. Modification of 2D layered materials through interlayer space expansion and surface functionalization has been extensively developed [1]. The most efficient and versatile approach to exploiting the flexibility of 2D materials is through liquid exfoliation to produce solutions of monolayers[2]. This has been tried by using surfactant-expanded precursors but required multi-step procedures resulting in low efficiency and yields [3]. Recently we have shown that high yield exfoliation can be achieved directly in high yield by soft chemical treatment with tetrabutyl hydroxide solutions [4]. The most interesting experimental procedures that lead to the obtaining of zeolite monolayers will be presented together with unambiguous evidence of zeolite unilamellar nanosheets in solution.

Exfoliated layered zeolites can be intimately combined in solution with other compounds to form chemical combinations at will and produce novel materials that have not been possible before. Zeolite nanosheet dispersions are particularly useful for preparation of various composite materials because of their solution-like character. They allow formation of hybrid catalyst simply by mixing zeolite layers and other active compounds. The examples are metal nanoparticles, metal oxide nanoparticles, and intimate mixtures of zeolites with different topologies (MWW/MFI) or liquid silicas.

The composites obtained with the use of the zeolite monolayers often displayed better catalytic properties than those obtained by conventional methods. Novel capabilities include top-down preparation of oriented discs and films.

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1252 - TWO DIMENSIONAL ZEOLITES ORIGIN EXPANSION AND PERSPECTIVES

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Two dimensional materials (2D materials) called sometimes as nanosheets, nanolayers, or simply layered materials represent a large group of inorganic, organic or hybrid materials with a high potential for applications in optoelectronics, spintronics, ion transport, biomedicine, energy harvesting and storage, and last but not least in catalysis. These materials possess exciting properties in different areas but also a high diversity of their chemical compositions.

In material science, layered materials are described as solids with highly anisotropic bonding. It means that two-dimensional sheets with thickness not greater than a few nanometers have strong internal bonds, usually covalent, but are only weakly attached to adjacent layers via e.g. hydrogen bonds, van der Waals interactions or intercalated molecules or ions. Owing to their distinctive structures with weak interlayer bonds, 2D materials are often suitable for intercalation reactions and expansion of the interlayer space. In the realm of layered solids, 2D zeolites represent a late and surprising entry as they were identified originally as exclusively 3D framework structures.

This special lecture, dedicated to the third Baron von Axel Cronsted Award, will focus on one particular group of two-dimensional materials – two dimensional zeolites, their origin, synthesis, characterization and perspectives. Various scientific achievements will be supplemented with a few historical comments on our cooperation and friendship.

So far about 10% of IZA approved different structural types of zeolites, i.e. over 20 out of 250, have been found in nanosheet forms but all are expected to exhibit the 3D-2D duality, possibly extending to 1D as exemplified by a recent example. In principle, they can be synthesized by both bottom-up (typical case) as well as top-down approaches, which exploit ordered structural weakness in certain crystallographic dimensions of 3D structures. 2D zeolites can be used in two directions, i) as extended building blocks for preparation of new materials (sometimes not accessible by other synthetic approaches) and ii) for adsorption, separation and particularly catalysis. Examples of both, synthetic and application, approaches will be discussed.

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1325 - POROUS TI BASED PHOTOCATALYSTS FOR ENVIRONMENTAL APPLICATIONS

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Recent advances in the development of highly active Ti-based nanoporous photocatalysts at the University of Antwerpen will be discussed. Synthetic procedures are explained as well as the photocatalytic performances of the materials in environmental applications for the gas-phase CO2 photoreduction, and the degradation of organic pollutants in aqueous phase. Key factors influencing the catalytic properties of the newly developed nanoporous photocatalysts are illustrated.

Research in the field of CO2 reduction has been growing rapidly over the last few decades, due to the increasing emissions of CO2 as one of the most dominant gasses causing global warming. The urge for developing efficient and sustainable CO2 capture and conversion technologies is therefore very high. Photocatalysis is a very sustainable technology for the reduction of CO2 since it can be performed at ambient temperature and pressure using sunlight. In this way, not only CO2 emissions are reduced but also solar energy can be converted into chemical energy. TiO2 is a very interesting photocatalyst for CO2 reduction since TiO2 is relatively cheap and non-toxic, and moreover, the energy levels of conduction and valence band thermodynamically enable the CO2 reduction reaction. However commercially available P25 titania has important drawbacks such as low surface area, and a high recombination rate of the photo-excited charges.

One of our strategies is to alter the properties of titania and to lower its recombination rate by forming composite structures with another semiconductor material. Suitable materials are Ferrites, having the general formula AB2O4 [1]. The ideal ferrite spinel structure presents all the octahedral sites (B) occupied by Fe3+, while the tetrahedral accommodates another metal. Apart from their own catalytic activity, these metals also serve as charge carrier traps increasing the life span of separated electron-hole pairs, and thus enhancing the photocatalytic activity of the catalyst. In our work, we investigated the use of mixed nanocomposites CoxZn1-xFe2O4@TiO2 for the photocatalytic reduction of CO2. Possible correlations and synergetic effects between the different cations in Ferrites systems and TiO2 nanoparticles were investigated and compared with the reference P25, for the photocatalytic CO2 reduction reaction [2] and also for the degradation of organic dye pollutants in aqueous phase.

A second strategy is the combination of Ti-based photocatalysts with noble metal nanoparticles. They can be used in photocatalysis both for plasmonic enhancement as well as serve as an electron sink for enhanced charge separation. In this context, platinum, palladium, silver and gold have proven very successful for different chemical transformations. In our work, we used a Ti-Beta zeolite as photocatalytic material for CO2 reduction because of its high surface area and isolated Ti (IV) species. To enhance the activity and improve the selectivity, the Ti-Beta zeolite was modified with Pt and Pd nanoparticles [3]. We used these nanoparticles in combination with a photoactive zeolite, activated by light in the UV-range and in this wavelength range the localized surface plasmon resonance (LSPR) states of Pt and Pd nanoparticles are excited. A combined effect of improved charge carrier separation, and a plasmonic contribution co-exist to improve the overall CO2 reduction rate in our work.

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1340 - GREEN AND RATIONAL SYNTHESIS OF POROUS METAL ORGANIC FRAMEWORKS AND THEIR NON CONVENTIONAL FORMS VIA MECHANOCHEMISTRY

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Modular porous materials based on coordination bonds (metal-organic frameworks, MOFs) have become a highly researched area of materials science. [1] For these versatile materials, the structure and properties can be readily altered by carefully choosing nodes and linkers. These materials are now widely studied for storage, separation, catalysis, sensing, light harvesting, quantum electronics, and other applications.[2] Several MOFs are also commercialized, but the standard synthetic procedures involving an excess of organic solvents and harsh conditions prevent their wider industrial application.

Here we present how mechanochemical reactions,[3], i.e. reactions between solid reactants induced by mechanical force, can be used for a rapid, sustainable, and controllable transformation of environmentally safe precursors into relevant microporous MOFs, such as HKUST-1, MOF-74 or zirconium-based MOFs of UiO and NU- families, or lead to the formation of their multivariate, amorphous, or hybrid derivatives (Scheme).[4] Direct monitoring of these processes revealed complex reaction pathways, often involving intermediate phases inaccessible from solution procedures.[5] It is possible to isolate and characterize these intermediates and use them for the controllable synthesis of non-conventional forms, such as various multivariate MOF-74, with interesting magnetic properties and potential for new applications.[6]

Keywords: mechanochemistry, porous frameworks, MOF composites, green chemistry, sustainability

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1342 - OPPORTUNITIES AND CHALLENGES OF ZEOLITE CATALYSTS IN THE TRANSITION TOWARDS SUSTAINABLE FUELS AND CIRCULAR ECONOMY

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Relevant advances have been achieved in past years for the replacement of fossil-derived resources with more sustainable feedstock by means of zeolite-catalysed transformations. Many of these routes use biomass raw materials, like triglycerides, lignocellulose and microalgae, with the aim of reducing significantly greenhouse gases emissions. Thus, triglycerides can be converted over zeolite catalysts by cracking, hydrodeoxygenation and decarboxylation into hydrocarbon mixtures within the gasoline and gasoil ranges. In the same way, catalytic pyrolysis of lignocellulose over zeolitic materials has been investigated extensively to produce a liquid organic fraction (bio-oil) that can be used as a source of both advanced biofuels and bio-based chemicals [1]. In particular, ZSM-5 zeolite has been widely studied in biomass catalytic pyrolysis due to its high selectivity towards aromatic hydrocarbons. In the same way, upgrading of bio-oil and biomass-derived platform molecules by a variety of routes, like aldol condensation, ketonization and hydrodeoxygenation, is being pursued over multifunctional catalysts based on zeolites modified with metal phases.

In addition to biomass resources, different types of wastes, like plastics and used tires, are of high interest as raw materials according to the circular economy paradigm. In particular, the strong environmental problems caused by the inadequate management of waste plastics has led to a renewed interest in their valorisation through different thermochemical conversion routes, such as catalytic cracking and hydroprocessing over zeolite-based catalysts [2]. The plastic pyrolysis oil so obtained can be further processed within refineries provided it contains a low halogen concentration. Accordingly, oil dehalogenation treatments are being also developed in many cases using zeolitic materials.

However, in spite of those achievements, the future role of zeolites in the transition towards a clean energy system and a circular economy is not secured due to the need of fulfilling very ambitious goals in a short period of time and the complexity of dealing with residues and wastes as raw materials. Thus, the European Union is at present considering to limit strongly by 2035 the manufacture of light road transport vehicles using conventional combustion systems, which means that the demand of gasoline and gasoil fuels might significantly decline in mid-term. Accordingly, the design of novel zeolite catalysts should be adapted to this new challenging framework [3, 4]. In particular, zeolite catalysts could have an important contribution in a number of strategic transformations, such as CO2 hydrogenation, alcohols/glycerol/bio-oil steam reforming, methane and ammonia decomposition, platforms chemicals C-C coupling, alcohol dehydration/olefin oligomerization and triglycerides hydroconversion.

For zeolitic catalysts to exhibit a suitable performance in those processes, a precise control of their properties will be required in terms of crystallinity/structure, accessibility (nano-, hierarchical-, dendritic- and 2D zeolites), multifunctionality (Brønsted/Lewis acidity and incorporation of metallic components) and lifetime [5].

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1351 - METAL AZOLATE FRAMEWORKS BIO COMPOSITES

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Metal-Azolate Frameworks (MAFs) are a subclass of Metal-Organic Framework (MOF) materials that have can form around different active biomacromolecules including proteins, nucleic acids, carbohydrates, and lipids.(1) The biocompatible synthesis conditions (ligand, metal salt, water) typically preserve the activity of the encapsulated biomacromolecule. The MAF matrix mitigates the detrimental effect of inhospitable environments. For example, zeolitic-imidazolate framework (ZIF) matrices offer increased stability to temperature, organic solvents, mechanical stressors chaotropic agents, and proteolytic agents.(2) For enzyme@ZIF systems, the control over the ZIF topology offers substrate access to the encapsulated biocatalyst.(2) For biotherapeutic@ZIF systems, the high loading capacity and the control over the topology enable tunable release profiles.(3) In this presentation, encapsulation protocols will be discussed, and relevant properties and limitations will be examined. Opinions about exciting opportunities for research will be disclosed.(4)

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1355 - AN OVERVIEW ON RECENT APPLICATION OF ZEOLITE TEMPLATED CARBON IN LIGHT GASES ADSORPTION AND (ELECTRO) CATALYSIS

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Carbon based materials are growing in attention for a perspective application in light gas storage/separation and electrocatalytic applications. Those two application fields are strategic in new energy scenarios supporting the strategy of energy-sources de-fossilization. In this concern carbon negative-replica of zeolite structure, so called Zeolite Templated Carbon (ZTC) is a new a class of carbon based-materials that couple the textural properties of the templated zeolites and the electrical conductivity of graphene-like structures. The ZTC structure is obtained via-carbonization of hydrocarbons (olefins, alcohols) into the pores of the sacrificial zeolite and after the dissolution of the silico-aluminate scaffold, a curved single-layer graphene fretwork is obtained. From the pioneeristic works in the late 90th's [1] different large pore zeolites (CHA, BEA) where used as templating media replica at different crystallinity level [2]. Beside the studies of the properties of these structures, also the applications have started to be proposed: from high performances capacitors [3-4] to light gases storage and separation [5-6] up to the really promising work on catalysis and electrocatalysis [7-8]. Moreover, the expansion of the fields of application requires an in-depth knowledge of the main characteristics of these "young" materials, with the aim of correlating the structural properties to the observed performances. In this context, the present contribution intends to illustrate the role of oxygen, always present on the surface of ZTCs. In particular, the C-O coordination offers the possibility of a wide range of functional groups, with different thermal stability, whose origin is still the subject of debate. The presence of these functionalities affects the performance in adsorption and catalytic applications. Furthermore, it is presented the possibility of functionalizing these materials, through the insertion of heteroatoms during the synthesis or with post-synthesis treatments, increasing the adsorption/separation capacity or can expanding the catalytic efficiency, both in "metal-free" and metal-on-ZTC supported catalyst. New evidence of the possibility of modifying and controlling the properties of ZTCs through deoxygenation techniques or modification of the characteristics of zeolite scaffolds will also be discussed, together with experimental techniques used to characterise in -depth the features of the obtained materials.

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1356 - GASOTRANSMITTERS DELIVERY VEHICLES FROM NANOPOROUS MATERIALS

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Localized administration of gasotransmitters, nitric oxide (NO) or hydrogen sulfide (H2S), can be a strategy to treat several human diseases, avoiding several side effects of systemic administration of NO or H2S donors. Nanoporous materials have the capability to store and release NO and H2S, and can lead to interesting therapeutic approaches for local delivery related with wound healing [1]. Nevertheless, two main challenges arise when these materials are used as carriers in biological media. One is the lack of stability of some structures in biological fluids, that leads to uncontrolled release and release of by-products. The other is the fast release rate of observed for many cases [1]. For certain applications, such as wound healing or tissue regeneration, these are major drawbacks. These problems may be solved by controlling the structure and the chemical environment in the pores, to obtain materials with slow-release kinetics and high stability in biological media, making them more suited for therapeutic applications as gas carriers. Some examples of different types of materials related with NO delivery will be highlighted in this presentation, demonstrating some breakthroughs [3-5]. For the release of H2S, although the less types of materials have been explored so far, the results already obtained are promising [6].
Another strategy that was explored to improve the stability of the compounds in biological media to achieve better biocompatibility, is the incorporation of materials in biocompatible polymers. Several types of polymers, such as polycaprolactone, polyethylene glycol and chitosan, were considered with different preparation methods. These composites have the also the important benefit of slowing, in some cases, the release rate of NO and H2S in liquid phase [7-9].

Although several important aspects still need to be validated for a future therapeutic application of these materials at clinical level, the perspective on the results obtained until is very encouraging and will motivate further research works related with wound healing or other application areas.

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1362 - ON SURFACE MOLECULAR FRAMEWORKS SYNTHESIS PROPERTIES AND FUNCTION

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Crystalline and porous molecular framework materials with specific encoded properties hold promise as a novel, highly tunable functional platform. Through the concepts of reticular chemistry, numerous two- and three-dimensional molecular frameworks with diverse structural, optical and electrical properties are in reach. [1, 2] On-surface deposition of molecular framework coatings is crucial for their utilization as active layers in advanced device-based applications including separation, sensing and optoelectronics. In addition to the variable backbone properties, gaining control over the molecular framework film morphology is of critical importance for achieving the intended functionality.[3]

Herein, the on-surface synthesis of molecular frameworks, namely metal- and covalent-organic frameworks (MOFs and COFs) as films and deposits is presented. For MOFs, vapor-assisted conversion (VAC), a versatile method for the deposition of thin films of both 3D and 2D MOFs, particularly for the metal (Ni2+, Co2+, Cu2+) catecholate, M-CAT-1 series, will be discussed. [4, 5] The films obtained by VAC feature thicknesses in the nanometer scale with a particular morphology, topography and roughness. Subsequently, M-CAT-1 films are implemented as active layers into devices to be tested for a variety of applications ranging from optoelectronics to waste water treatment.[6, 7] For the latter, ultrahigh flux separation of oily pollutants from water is achieved with a filter mesh decorated with MOF nanoscale architectures. For COFs, the in-situ thin film synthesis approach will be described as a reliable and well-established methodology for the synthesis of COF thin films. Here, the synthesis of novel layered thiophene-extended benzotrithiophene-based (BTT) COFs as highly oriented and crystalline thin films and their respective directional electrical conductivity will be illustrated, where BTTCOFs show enhanced in-plane electrical conductivity compared to out-of-plane electrical conductivity.[8]

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1363 - CATION MEETS GUESTS – HOW CATIONS CAN BE EXPLOITED FOR GAS PHASE SEPARATIONS IN FLEXIBLE ZEOLITES AND METAL ORGANIC FRAMEWORKS

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Nanoporous zeolites and metal-organic frameworks (MOFs) are widely used and studied for gas separations. While even apparently rigid zeolites and MOFs exhibit some inherent flexibility, some members of these families significantly alter their pore accessibility, shape and size significantly upon external stimuli such as the temperature or the uptake of guest molecules. This can lead to phenomena that can either be beneficial or detrimental for separations. Therefore, understanding the molecular level phenomena and mechanisms is essential to exploit these phenomena. Molecular simulation in combination with experimental techniques provides a powerful tool to do exactly this. In this talk I will use two examples from our recent work to elucidate the role that cations can play.
In zeolite RHO, extraframework cations are present in the eight membered rings (8MR) occupying the spaces between cages and act as gate keepers, selectively allowing, for example, the uptake of CO2 but restricting the uptake of CH4.1 Here I will show how our simulations revealed the whole mechanism of how the guest molecules interact with cations, moving them out of the way for CO2 thus opening up a diffusion path while staying put for CH4.

SHF-61 is a doubly interpenetrated metal organic framework composed of indium centres and aminoterephthalate ligands charge-balanced with cations inside the pores.2 In contrast to other MOFs exhibiting wine rack-like flexibility such as MIL-53 in this particular MOF the breathing behaviour and therefore the pore size can be fully tailored through partial activation or solvent exchange before activation. Here our simulations complement a wealth of experimental observations and provide an explanation how the cations interacting with solvent molecules is key to wedging the pores open and thus allowing or prohibiting the opening of the pores.

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1375 - NMR AS A TOOL IN POROUS MATERIALS INVESTIGATION

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Nuclear Magnetic Resonance (NMR) spectroscopy is a powerful tool for studying porous materials and comprehending their atomic and molecular structure, composition, and dynamics. NMR provides valuable insights into the local environment and molecular interactions within the pores of these materials. By utilizing advanced solid-state NMR techniques, spatial information regarding nuclear proximities within the structure can be obtained.

Herein we present several case studies that demonstrate the practical application of NMR in the field of porous materials. In 2015, our research demonstrated the utilization of proton spin diffusion build-up curve modeling, which provided important insights into the distribution of linkers within the mixed-linker metal-organic framework ML-DUT-5 [1]. This research gained significant attention within the scientific community and led to the study of structural defects in UiO-66(Zr) [2,3], as well as the monitoring of structural changes during the melting of ZIF-62 [4,5]. Additionally, 2-dimensional heteronuclear and homonuclear correlation spectra play a crucial role in providing qualitative information, particularly when studying encapsulated guest molecules. Our emphasis lies on the investigation of zeolite Beta for various applications, including the study of its effectiveness in removing PFOA, a prominent pollutant in wastewater [6]. We will illustrate the contribution of NMR in this research. Furthermore, we have also explored the mechanisms of water filling and the origins of step-like water sorption curves in microporous aluminophosphates, such as AlPO-34 and AlPO-LTA, which exhibit exceptionally high water-sorption-based heat-storage capacity [7].

These case studies not only showcase the versatility of NMR as a tool for studying porous materials but also highlight its potential in providing valuable insights that can guide the design and synthesis of new materials with enhanced properties.

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1376 - BIG DATA SCIENCE OF POROUS MATERIALS

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The synthesis of metal-organic frameworks (MOFs) has witnessed remarkable progress over the past decade, resulting in a vast repository of over 100,000 MOF-like structures documented in the Cambridge Structural Database (CSD). This wealth of data presents a unique opportunity to leverage data-driven methodologies to gain deeper insights into the properties and behavior of porous materials.[1,2]

In this presentation, we delve into the application of data science methods---from hand-tuned features to large language models [3,4]---to the design of porous materials. We give some examples of how these techniques can be used to predict properties such as color[5] and oxidation states of MOFs.[6]

This talk highlights the transformative potential of big data science in advancing our understanding of porous materials, specifically MOFs. By leveraging the power of data-driven methodologies we not only enhance our fundamental knowledge of these structures but also pave the way for tailored design and discovery of MOFs with desired properties across a wide range of applications.

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1377 - RECENT ADVANCES AND FUTURE CHALLENGES IN ZEOLITIC MATERIALS

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Zeolites are crystalline microporous materials that are widely used in the petroleum refining and petrochemical industry as catalysts and molecular sieves. Through the years, the properties of zeolitic materials were modified to meet different challenges; for instance, new feedstocks, changes in the supply-demand chain, changes in product demands, and environmental needs. However, the ongoing energy transition requires zeolites with properties that go far behind their comfort zone and also points to the need for new zeolitic materials.

The first part of the lecture is devoted to the mechanism of zeolite formation by a top-down approach. The zeolite formation mechanism is studied by the unbiased dissolution of well-shaped zeolite crystals, revealing different stages of zeolite growth. The growth history, from the slow growth in the last stage due to the low supersaturation to the abundant zeolite nucleation in the initial highly super-saturated period, is monitored. This top-down approach allows performing “zeolite archeology” on a single crystal level. The practical aspects of the presented top-down approaches for designing zeolite crystals with pre-determined properties will be discussed. The post-synthesis framework modification, which allows a fine-tuning of zeolite properties, is an integral part of this topic and will be discussed in depth.

The second part of the talk is devoted to the need for new zeolitic materials. More specifically, two sub-groups of zeolitic materials will be addressed - the thermaly stable extra-large pore zeolites with an example based on ZEO-1, and the clatrasils as gas storage materials with substantial pore volume, but with poor diffusivity. The development of “zeolitic ice”, i.e., the synthesis of water-based gas hydrates structurally identical with MEP-, MTN- and DOH-type will be presented, and their gas storage abilities discussed.

SPECTROSCOPY AND MICROSCOPY OF ZEOLITES AND METAL-ORGANIC FRAMEWORKS AT WORK

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Recent two decades have witnessed the introduction of powerful spectroscopy and microscopy methods for the characterization of crystalline porous materials, such as zeolites and metal-organic frameworks (MOFs), at previously unattainable spatial resolution and sensitivity. Maybe as important is to realize that each of these characterization methods possess different field-of-views (FOVs). These distinct differences in FOVs allow to gather detailed information of these functional porous materials at different length scales, starting from the level of an individual body (e.g., a catalyst particle, including binder materials, such as alumina, silica, and/or clay) in its full integrity down to the level of a single atom (e.g., Al or C) or molecule (e.g., a fluorescent molecule) within an embedded zeolite or MOF aggregate. This opens the door for advanced multiscale characterization studies of functional materials.

The goal of this lecture is to illustrate how a combination of novel spectroscopy and microscopy methods may help in understanding the functioning of zeolites and MOFs at work. The following analytical techniques will be discussed: soft and hard X-ray microscopy and tomography (e.g., STXM, TXM, and X-ray holotomography), single-molecule and confocal fluorescence microscopy (SMF and CFM), UV-Vis micro-spectroscopy, atom probe tomography (APT), and photo-induced force microscopy (PiFM). The lecture presents this multiscale micro-spectroscopy approach by making use of several showcases, namely thin-films and single crystals of MOFs (e.g., formaldehyde and ethylene conversion), thin-films of zeolite ZSM-5 (e.g., determination of diffusion coefficients in straight and sinusoidal channels), millimeter-sized zeolite-containing catalyst extrudates and spheres (e.g., Fluid Catalytic Cracking, FCC catalyst particles), and micrometer-sized zeolite SAPO-34, SSZ-13, Beta, and ZSM-5 (e.g., APT to determine Al and C zoning). Next to diffusion and reactivity of single molecules, attention will be focused the elucidation of reaction and deactivation mechanisms. The pros and cons of this multiscale characterization approach are discussed, including some directions for future research.

CATEGORY: ADVANCED SYNTHESIS (ZEOLITES, ZEOLITE-LIKE MATERIALS, MOFS, OTHER POROUS SOLIDS)

1012 - ZIF 8@PEO COMPOSITE AS A NEW GENERATION OF CONVERSION COATINGS INSIGHT INTO THE STRUCTURE

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Nowadays, due to severe environmental pollution, serious waste of resources and enormous losses for the world economy, corrosion protection stands out as one of the most important industrial tasks. An effective way to improve corrosion resistance consists in the formation of protective coatings on the surface of metallic materials. In this context, plasma electrolytic oxidation (PEO) found broad application as a multi-purpose technique to create effective corrosion and wear resistant coatings on various metallic substrates [1]. The oxide layers formed via PEO approach are usually hard and demonstrate strong adhesion to the substrate. However, their main disadvantage is the presence of numerous open pores and cracks, which significantly compromise barrier protective properties. Several methods were developed to overcome this obstacle, among which post synthesis modification was the most effective [2]. Recently, thanks to exceptional properties, metal organic frameworks (MOF) also emerge as perspective materials for the corrosion protection [3]. Moreover, their features also highlight the potential of MOF for effective sealing of pores in PEO layers.

For the first time, a novel composite coating containing PEO layers and ZIF-8 MOF was formed [4]. It was prepared via controllable transformation of a PEO layer formed on Z1 zinc alloy into ZIF-8 MOF in the presence of 2-methylimidazole (2-HmIm) as organic linkers. Cross section analysis, glow discharge optical emission spectroscopy (GDOES) and nano-focused synchrotron X-ray diffraction demonstrated that varying of synthesis parameters, the ZIF-8@PEO coating with different distribution of ZIF-8 through PEO layer can be prepared. Based on the results of laser scanning microscopy, the surface smoothing was observed with increasing the degree of the PEO-to-ZIF-8 rearrangement.

XRD, SEM, GDOES and nano-focused synchrotron XRD analyses demonstrated the multi-stage mechanism of the process, which starts with partial dissolution of PEO layers accompanied by the formation of new defects on the surface. Then, released zinc ions react with organic ligands forming ZIF-8, whose crystallization begins on the PEO surface and gradually spread into the internal PEO pores. It results in a sealing of the PEO pores and defects by ZIF-8 and, consequently, in formation of a compact protective coating. The final ZIF-8@PEO composite coating possesses exceptional physical-chemical properties, as it combines the features of both: PEO ceramic parental layer and formed ZIF-8 metal organic framework.

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1013 - SINGLE WALLED ZEOLITE NANOTUBES

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Synthesis of zeolites with hierarchical porosity that allow micropore access to a wider range of molecules has been a recent research focus. Early approaches included post-synthesis treatments to etch mesopores into zeolite crystals. More recently, new SDAs have been used to create 2D zeolite nanosheets interspersed by mesoporous regions, yielding nanosheets of several zeolitic topologies such as MFI, FAU, AEL and MWW. Here we describe the first synthesis and structural characterization of a quasi-1D hierarchical zeolite, specifically a single-walled nanotube that has a microporous zeolitic wall enclosing a central mesoporous channel [1].

TEM images, X-ray diffraction, electron diffraction, nitrogen physisorption, 27Al and 29Si NMR all provide data consistent with the formation of crystalline microporous domains in concert with mesoporous domains. High resolution electron microscopy images a crystalline structure that includes ~6 Å pores in the nanotube walls and a central mesoporous channel of 3 nm inner diameter. The structure of a circumferential building unit ("CBU") was imaged. The CBU consists of 28 T-atoms arranged in three types of zeolite composite building subunits: one MTW-type, two BEA-type, and two MOR-type. Repetition of ten CBUs leads to the nanotube circumference. The CBUs are connected through a 5MR, and not a 6MR as in zeolite beta. Connection through 5MR in the nanotube enforces a ~36° rotation of each CBU relative to its neighbors – this is important for closure of the cylindrical sheet (nanotube). The terminal T sites in the nanotube walls can also act as branching points to form fused nanotubes. The nanotube circumference structure is then replicated in the axial direction to obtain the complete structure, which matches the ADF-STEM/iDPC images. The final structure, when geometry-optimized with COMPASS-II force field, shows physically reasonable bond lengths, angles, etc. Simulated and experimental PXRD patterns are in very good agreement. A remarkable feature emerges naturally from the arrangement of the CBUs. Due to the curvature of the tube, the two wall surfaces have different topological structures. There are 10MR micropores on the inner surface and 12MR micropores on the outer surface. The outer surface is built from 4MRs, 5MRs, and 6MRs leading to 12MR micropores: identical to a layer of zeolite beta. The inner surface is built from only 5MRs and 6MRs leading to 10MR micropores: identical to an AC-plane layer of MFI. Thus, the nanotube wall is a unique "atomic-scale" hybrid of zeolites beta (polymorph B) and MFI.

1027 - OPTIMIZING POROSITY AND ACIDITY OF FAUJASITE ZEOLITES FOR SUGAR TRANSFORMATION

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Dwindling crude oil reserves and climate change mitigation have raised extensive studies on biomass which is one of the alternative resources. Biomass provides sugars such as glucose, fructose and xylose, well-known intermediates in the conversion of biomass into added value chemicals. [1] 5-HMF, one of the platform chemicals, is obtained from the dehydration of fructose and can be further transformed into biofuel and bioplastic. For this sugar transformation, acid catalysis is of importance. Faujasite zeolite is interesting since their strong acidity and relatively large pores have been indispensable for fluid catalytic cracking process. Nevertheless, zeolite remained microporous material causing diffusion limitation with bulky substrates. Besides, sugars have been reported to have a diffusion suffering inside microporous zeolite.[3]

With the aim of overcoming the chronical diffusion problem, we modified microporous zeolites to hierarchical zeolites. We studied the impact of Si/Al ratio on post-modification with 3 commercial USY zeolite with different Si/Al ratio (6, 16 and 27 respectively). The modification method is acid leaching using oxalic acid and base leaching,[3] using tetraalkylammonium hydroxide (TAAOH) of different alkyl chain lengths, from C1 to C4. Since as-synthesized zeolite Y contains more silicon than aluminum, desilication generates more pronounced mesopores rather than dealumination. However, desilication takes place in the alkaline medium where Al prevents the extraction of the framework silicon atom from OH- hydrolysis. Thus, for the zeolite with low Si/Al ratio dealumination should precede desilication, to lower resistance to base treatment.

We analyzed alterations of properties after acid or/and base treatment: porosity, acidity, crystalline structure, Si/Al distribution, and Al coordination. We found that the ideal Si/Al ratio of USY zeolite for base leaching using TAAOH is between 15 and 30. The TAAOH tailors pore size and protects the zeolite structure differently depending on alkyl chain length. Propyl chains provided the best compromise between creating a large volume of mesopores and preserving micropores. In the case of the starting zeolite with Si/Al=27, mesopore volume increased from 0.322 ml/g to 0.781 ml/g while micropore volume slightly decreased from 0.251 ml/g to 0.235 ml/g. On the other hand, base leaching was not effective for Si/Al=6 due to the high content of aluminum species. To remove aluminum, we varied the concentration of oxalic acid which effectively controls the level of dealumination from Si/Al=11 to 37. Subsequently, base treatment was successfully applied on differently dealuminated zeolite. Consequently, this method allowed to control mesopore volume from 0,323 ml/g to 1,032 ml/g compared to 0,267 ml/g of parent material. Therefore, the Si/Al ratio of starting material is the most important criterion to debut the first treatment, which is acid or base leaching.

To evaluate modified zeolites, we conducted the catalytic dehydration of fructose to 5-HMF and attempted establishing a relationship between the catalytic activity and zeolite properties. Qualitatively, we found a positive tendency of Brønsted acid sites concentration, specific surface area and microporous volume for the reaction rate, while Lewis acid site concentration has a negative tendency. Concerning mesopore volume, modified zeolite exhibited better catalytic performance only if crystalline structure was preserved. This reveals that to optimize the modification method for 5-HMF the preservation of zeolite intrinsic properties should be a precondition.

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1055 - ZEOLITE BASED HYBRID STRUCTURED ADSORBENTS WITH TUNABLE MORPHOLOGY AND ARCHITECTURE THROUGH SYNERGISTIC COMBINATION WITH POLYIMIDES

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The trends in the utilization of adsorption technology for addressing variety of challenges related to energy, water and environut problems are ongoing. The past works reveal the significance of progresses in the synthesis of new adsorbents, modification and tuning of existing adsorbents, fabrication techniques as well as integrating adsorbents into the process unit for target applications. These may be regarded as the prevailing research directions [1].

Along with the widespread use of established inorganic adsorbents, an attractive concept is exploiting the advantages of polymers as adsorbents. In this regard, polymers possessing specific functionalities have potentials for offering affinity and selective adsorption [2]. Aside from this, it is demonstrated that the porous structure and the morphology of the polymeric adsorbents play essential role in the ultimate performance [3]. Therefore, an attractive approach would be to combine the synergistic advantages of both types of inorganic and organic materials for development of high performance adsorbents [4]. In this strategy, the adsorption capacity of inorganic adsorbents can be integrated with the processability of polymers for the fabrication of hybrid structured adsorbents, in the form of pellets, films or monoliths for instance. In the new form, the limitations in the handling of powder adsorbents are eliminated as well. However, proper selection of the base materials and the procedures used for such developments are important in order to make a successful outcome. It is also essential to ensure that the active sites of the adsorbents remain accessible to the adsorbates by promoting highly porous matrix with large enough surface area.

The present research aims to share the results of our attempts towards extending applicability of zeolites as one of the popular adsorbents in combination with polyimides. For this purpose, zeolite 13X was selected as the representative adsorbent and Matrimid served as the polymer candidate. The pelletized adsorbents were fabricated by the in-house developed method of non-solvent induced phase separation in different materials including water, alcohols (ethanol and methanol) and a combination of them. In addition, some of the samples were successfully fabricated in ambient atmosphere with the aid of a suitable solvent. Successful fabrication of hybrid adsorbents was achieved by zeolite loading from 25 wt.% to as high as 90 wt.%. The morphology and microstructure of the as-fabricated pellets were characterized using scanning electron microscopy and other techniques, in order to gain insights on the mechanism involved in the fabrication process. The findings are interesting especially since it revealed that the process was dependent of the adopted steps and other factors taken into considerations. In this paper, we discuss the findings and the relevant mechanisms about the fabricated adsorbents especially with regards to the adsorption characteristics with respect to target gases. In addition, the importance and consequences of selection of non-solvent medium and the roles in the process of solidification of the entire structures and pore formation are explained. The results provide a unique platform enabler for fabrication of desired hybrid structured adsorbents from the variety of candidate materials for intended applications.

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1063 - STRUCTURAL TRANSFORMATION OF IWV INTO NEW ZEOLITE

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The recently developed ADOR method is the multi-step strategy for the generation of new daughter zeolites by post-synthesis treatment of known parent zeolites [1]. Summarizing the examples reported up to now, ADOR is applied to germanosilicate zeolites consisting of stable Si-rich layers connected by double-four-ring units (D4Rs) predominantly occupied by Ge atoms (> 4 Ge atoms of 8 atoms in D4R unit). The core of the strategy is the selective transformation of D4R units along with the preservation of structural fragments, such as dense or porous layers.

Similarly to traditional zeolite synthesis, ADOR transformation (i) includes the formation of several intermediate phases and (ii) proceeds with the lowering of free energy if a less feasible optional framework is not stabilized, for example, by the presence of an organic structure-directing agent [2,3].

IWV belongs to a family of zeolites that potentially can be but has not yet been transformed by ADOR. Like many other chemically labile framework materials, including germanosilicates, it is susceptible to water. We found that the output of IWV water-assisted deconstruction is, first, dependent on the intrinsic characteristics of the parent zeolite such as the Si/Ge ratio in the framework and the morphology of its crystals. Furthermore, the output can be controlled by balancing the reaction rates of sub-processes (D4R units dissolution, layers degradation, reconstruction) upon structural conversion.

Design the characteristics of parent zeolite and optimization of ADOR conditions, including the polarity of reaction medium, allowed us to catch a phase of new zeolite possessing the framework structurally related to the initial IWV. Using seed-assisted crystallization of IWV followed by its gentle transformation in the water-alcohol system, the highly crystalline daughter zeolite IPC-20 was produced, while its structure has been solved using precession-assisted 3-dimensional electron diffraction. The IPC-20 structure contains the S4R units instead of the D4R units of the parent material, while the denser silicate layers of a topology similar to those of IWV stay practically intact.

Adsorption and spectroscopic characterization evidence negligible layer destruction phenomena upon the whole sequence of transformations. This indicates the efficiency of proposed method for preparation of highly crystalline zeolites by post-synthesis approaches based on transformation of chemically labile frameworks.

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1072 - TUNING THE PROPERTIES OF DENDRITIC ZSM 5 ZEOLITE SYNTHESIZED BY PROTOZEOLITIC NANOUNITS FUNCTIONALIZATION WITH AMPHIPHILIC ORGANOSILANES

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Silica-based materials with dendritic morphology have attracted recently much attention due to their remarkable accessibility provoked by the presence of a highly interconnected radial morphology [1]. However, their intrinsic amorphous nature limits their use in many industrial reactions involving harsh conditions. On the other hand, zeolites are well-known crystalline microporous aluminosilicate materials, having a large variety of industrial applications as catalysts, adsorbents and supports. The accessibility of conventional zeolites is limited by their micropore size, restricting their use in reactions involving bulky molecules. Thereby, a number of strategies have been developed for tuning the accessibility of zeolites, mainly based on the synthesis of nanometric or hierarchically porous zeolites. In this way, the development of zeolitic materials with dendritic morphology could be a hallmark in the path for the improvement of their accessibility.

This communication discloses how the crystallization of silanized protozeolitic units' method [2] is an efficient strategy for obtaining dendritic zeolites when advantageously combined with amphiphilic organosilanes. Thereby, dendritic ZSM-5 has been synthesized using four different amphiphilic organosilanes with a base molecular formula of (R)(CH3)2-N+-(CH2)3)-Si(OCH3)3, being R = C10, C14, C18, and C22 alkyl chains following the procedure published elsewhere [3] under two crystallization temperatures (150 ºC or 170 ºC).

Characterization of the crystalline samples recovered after the hydrothermal crystallization indicates that there is a hydrocarbon length optimum between C14 and C18 for obtaining ZSM-5 zeolites with dendritic morphology. This finding has been connected with the formation of a highly ordered mesophase during the gel silanization step, which seems to act as precursor of the dendritic zeolite formation. The use of C10 organosilane results in a hierarchical ZSM-5 zeolite, in which the dendritic nanoarchitecture is slightly developed, exhibiting a relatively broad mesoporosity centred at 5 nm. On the other hand, the C22 organosilane leads to a very heterogeneous sample formed by a mixture of conventional and hierarchical ZSM-5 zeolite crystals, as well as with some amorphous phase. Regarding to dendritic samples, it has been found that the BET surface area decreases as the temperature of crystallization temperature increases. The best textural properties were obtained for the C18 – 150ºC sample, which displays a BET surface area of 580 m2·g-1 and a total pore volume of 0.91 cm3·g-1. Likewise, the dendritic ZSM-5 samples crystallized at 150ºC exhibited the best catalytic activity when tested in the aldol condensation of furfural with cyclopentanone, which is a relevant reaction for the production of advanced biofuels.

These results highlight the great potential of dendritic ZSM-5 zeolites as catalysts in reactions involving bulky species due to their outstanding accessibility and how their textural properties can be tuned by adjusting both the chain length of the amphiphilic surfactant and the crystallization temperature.

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1086 - ENGINEERING HIGHLY POROUS ALUMINA MATERIALS FOR CATALYSIS AND ADSORPTION

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Alumina is an important industrial material, widely applied in catalysis, adsorption and separation. However, the poor textural properties of the traditional alumina have limited its application in catalysis. Therefore, a considerable effort has been devoted to the preparation of mesoporous alumina with new structural properties. In our group, a mesoporous pure γ-Al2O3 without amorphous domains was synthesized using a cation-anion double hydrolysis (CADH) approach [1]. This approach was further modified as the hydrothermally promoted double hydrolysis (HPDH) approach [2], leading to the preparation of monodispersed colloidal alumina-based particles. Besides, mesoporous alumina microfibers with controlled morphology via a copolymer controlled homogeneous precipitation (CCHP) approach were prepared [3].

These different types of alumina materials show better performance than that of traditional commercial alumina in a variety of catalytic reactions and adsorption applications, involving propane dehydrogenation, cyclohexanone condensation, heavy oil catalytic cracking, reaction adsorption desulfurization, etc. [4-8]. The excellent catalytic performance of the obtained alumina is mainly attributed to its superior pore structure and unique surface chemical properties.

However, most of the previous appraches involve the use of costly organic templates, which is costly and the removal of templates by calcination releases polluting emissions. What's more, as the organic templates are not able to generate intracrystalline porosity, there exists a contradiction between high surface area and large pore volume. Those materials with large pore volume commonly exhibit a low surface area. Recently, we prepared alumina nanofibers with both large pore volume (> 2.8 cm3/g) and high specific surface area (> 650 m2/g) by inorganic ion intercalation method in the absence of organic templates. The alumina nanofibers exhibited a superior catalytic performance than that of commercial alumina in the fluid catalytic cracking (FCC) of vaccum gas oil (VGO). Using this alumina nanofiber as the matrix, the VGO conversion of FCC catalyst was increased by 2.21% with the yield of gasoline enhanced by 4.40%.

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1091 - ALUMINIUM AND ACID SITE EVOLUTION DURING ZEOLITE CRYSTALLIZATION AND THERMAL ACTIVATION

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Despite extensive tuning of zeolite catalyst, little is known on the synthetic origin of acid sites and their distribution at the sub-nanoscale. Even more, the effect of calcination is often unconsidered. This work demonstrates bottom-up rational selection criteria for synthesis of SSZ-13 (CHA) and ZSM-5 (MFI) with tuned Al and acid site distributions. It is demonstrated that Al and acid siting change during prolonged synthesis and during thermal activation. Many recent findings suggest that zeolite catalysis is influenced by synergistic effects (BAS-BAS; BAS-LAS) derived from acid site proximity or Al distribution.[1] Next to adequate post-synthetic treatments,[2] delicate engineering of zeolite crystallization (synthesis) is possible with control over crystal dimensions, morphology and charge deficit. Hence, synthesis is an important consideration when deliberately making application oriented materials with tuned Al and acid site proximity.

In our work, five crystallization systems are studied yielding ZSM-5 (MFI) and SSZ-13 (CHA), made either via interzeolite conversion or conventionally. [3,4] Synthesis evolution is tracked for stoichiometrically identical synthesis systems. This data demonstrates variable tendencies to assemble Al within the forming OSDA-zeolite composites.[4] Overall, Al was identified as key component during all stages: (FAU) dissolution, nucleation, assembly and maturation. The latter is generalized through an in-depth comparison with literature.[5] Single-parameter variations applied during synthesis of siliceous SSZ-13 showed that both kinetic and thermodynamic components influenced Al distribution.[3] Most significantly, it was found that internal arrangement of Al in SSZ-13 still evolves with synthesis time. The extent of synthesis evolution varies dependent on the synthesis system (OSDA-zeolite combo), which was previously unreported in literature. TPA/Na containing ZSM-5 has a strongly evolving DCC, whilst no DCC evolution is detected over (oven) time for TMAda/Na containing SSZ-13.[4] Our work adds novel insights on the synthesis processes that regulate the final acid site distributions within zeolites by taking into account the mobility of ionic charge. It is proposed that internal rearrangement of Al occurs at the level of cages towards more thermodynamically favored Al (charge) separation.[4] Furthermore, Al distributions are also found to change with calcination. We engineered a low-temperature ozone activation process for zeolites.[6] In parallel to Al mobility upon prolonged synthesis, elevated calcination temperature also affects the internal Al distributions, as well as Al speciation. A picture is drawn how Al speciation evolves with activation temperature, also taking into account the synthesis-specific reality (crystal size, stability, etc.).[7] Understanding the mostly unconsidered effect of ‘synthesis + activation temperature’ may not only help to explain conflicting literature reports, but it may also significantly enlarge the toolbox for bottom-up rational engineering of future catalysts.

1106 - MFU 4 TYPE SCAFFOLDS FEATURING OPEN BIDENTATE BIBENZIMIDAZOLE COORDINATION SITES

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Host-guest assemblies built from metal-organic frameworks (MOFs) featuring additional binding sites have proven highly beneficial for catalytic applications like biomass conversion or photocatalytic CO2 reduction [1-2]. Further enhancements of such systems are envisaged from the coupling of active hosts and guests leading to multi-step catalytic processes, including photocatalytic redox cascades. For this, multi-metal-site derivatives of CFA-19 ([Co5Cl4(H2-bibt)3]; Coordination Framework Augsburg University-19) and CFA-19-Tp ([CoII5Cl0.4Tp3.6(H2-bibt)3]; Tp= trispyrazolylborate), which are constructed isoreticular to MFU-4 with the novel H4-bibt (H4-bibt= 1,1',5,5'-tetrahydro-6,6'-biimidazo[4,5-f]benzotriazole) linker, are investigated. Thus, combining free bibenzimidazole coordination sites with the functional Kuratowski-type secondary building units (SBUs) known from literature [3-6]. In contrast to generic bipyridines often incorporated in MOFs, the bibenzimidazole backbone presumably allows for stronger binding of metal ions via additional deprotonation. This deprotonation was proven by the reaction with ZnEt2, which resulted in ZnEt moieties at the bibenzimidazole sites of the ZnEt@CFA-19-Tp framework. In addition, incorporation of accessible MBr(CO)3 (M= MnI, ReI; MBr(CO)3@CFA-19-Tp) sites, which are well-known for photo- and electrocatalytical CO2 reduction, was proven by single-crystal X-ray diffraction and investigated in detail via Argon adsorption, PXRD, VT-PXRD, IR, DRIFT, EDX, ICP-OES, and TGA measurements. Hereby, the MnIBr(CO)3@CFA-19-Tp revealed a complete thermal CO dissociation from the MnBr(CO)3 moiety, which provides us with highly coordinatively unsaturated open metal sites in this framework that can be used for the binding and activation of small molecules. [7]

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1113 - PROBING THE ACTIVE SITES OF DEFECT ENGINEERED UIO 66 BY FTIR SPECTROSCOPY

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UiO-66 is a metal-organic framework applied in catalysis, gas storage, drug delivery, etc. [1]. Zirconium ions in this MOF are bonded via bridge µ3-O and µ3-OH groups, forming Zr6O4(OH)4 clusters. During thermovacuum treatment, zirconium clusters lose 2H2O molecules and transform to Zr6O6 with six µ3-O groups. Strong Zr-O covalent bonds and high coordination numbers make UiO-66 extremely tolerant to the high concentration of defects in the structure. The coordination modulator approach is one of the ways to introduce defects. According to this technique, monocarboxylic acid (modulator) competes with terephthalic acid for Zr coordination [2]. Because the modulator has only one carboxylic group, it is not able to connect two Zr clusters. Coordination of the Zr-site with monocarboxylic acid creates defect sites in two opposite Zr-clusters forming a missing-linker defect. Consolidation of missing-linker defects (high modulator concentration) results in the generation of missing-cluster defects. Defects modify UiO-66 properties in different ways [3]. However, direct observation of defect sites is still a challenging task.

Here we present a comparative IR spectroscopic study of UiO-66 with and without defects. Three samples were obtained using solvothermal synthesis. UiO-66-0BA sample was produced without a modulator and resulted in aggregated nanoparticles. UiO-66-10BA was synthesized with 10 eq of benzoic acid resulting in highly porous nanoparticles with missing-linker defects. UiO-66-60BA was obtained with 60 eq of benzoic acid and contained highly porous micron crystals with missing-cluster defects. For the IR studies, the sample pellets were activated at 275 oC in order to remove DMF residues, then hydroxylated and evacuated at r.t. With all samples, we detected µ3-OH groups (3677 cm-1). Low-temperature CO adsorption showed these OH groups are of weak acidity (ΔνOH = 74-79 cm-1) and are the only CO adsorption sites. However, the use of CD3CN as a probe (able to replace water) revealed some Zr4+ sites, but only with the UiO-66-0BA sample. This was associated with the imperfection in the UiO-66 framework due to the fast nucleation. The dehydration process of the Zr-clusters was followed as a function of the evacuation temperature. CO as a probe indicates a slight increase in OH's acidity with dehydroxylation. No Zr4+ sites were detected on UiO-66-10BA and UiO-66-60BA samples even after 275 oC evacuation. This shows that Zr4+ sites remain linked to benzoate groups and are thus coordinatively saturated. A small amount of Zr4+ sites were detected with the UiO-66-0BA sample; the same was observed at r.t. by CD3CN.

Interestingly, Zr4+ sites were detected by CD3CN with all samples evacuated above 150 oC, and the amount of these sites increased with the dehydroxylation degree. Because these sites were invisible by CO, we stress that CD3CN, being a stronger base than CO, causes some structural changes in the zirconium clusters. Thus Zr4+ ions originally holding OH groups can be tested.

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1120 - THE IMPACT OF INITIAL GEL PROPERTIES ON THE INNER ARCHITECTURE AND CATALYTIC PERFORMANCE OF ZEOLITES

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The performance of zeolite catalysts intrinsically depends on the structure and chemical composition of crystals. Great efforts have been put into the investigation of the factors affecting the macroscopical properties of zeolite crystals, including the size, morphology, acidity and porosity, etc.1. However, less attention has been paid to the properties of the initial gel that play a decisive role in the formation of the final zeolite products2. In our recent work, two important phenomena, the defect-zoning and the Al-zoning, in pseudo-single ZSM-5 crystals by detailed study of the crystallization process were revealed.

Here, we report the synthesis of two ZSM-5 zeolites through the alternation of the mixing order of Si and Al sources3. The change of the mixing order did not impact the bulk composition, porosity, and acidity properties, however, it resulted in a substantial change of the inner architecture of the zeolite crystals (Figure 1). A comprehensive study of the zeolite structures was conducted by both the top-down deconstruction of the as-synthesized zeolite crystals using the chemically unbiased etching, and the bottom-up tracking of the crystallization history. The ethylene dehydroaromatization (EDA) was selected as a model reaction to study the intimate structure-performance relationships in the zeolite catalysis. The two zeolite samples with different inner architecture showed obviously different catalytic activity, products selectivity and coking behavior in the EDA reaction.

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1131 - BEYOND INTERZEOLITE CONVERSION ESTABLISHING CLOSE CONTROL OVER AL DISTRIBUTIONS IN SSZ 13 ZEOLITE BY REGULATION OF CRYSTALLIZATION KINETICS

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Zeolites have long been seen as difficult to modify due to their synthesis being a sequence of complex and reversible coupled dissolution-precipitation mechanisms that are still not entirely understood by the community. As a result, most of the research has been focused on single parameter variations, in an effort to exert control over parameters such as the Si/Al ratio, topology or crystal size.
However, recently control over Al distributions, more precisely the divalent cation capacity (DCC), has been gaining more interest as it was shown to be a key performance indicator for many zeolite catalysed reactions such as the partial oxidation of methane[1] or the dehydration of methanol[2]. A powerful tool in the control over Al distributions is interzeolite conversion (IZC), in which a crystalline zeolite is used as the Si and Al source for a different framework. It was shown that due to the fast crystallisation kinetics, in combination with the densification of Al rich oligomers in a pre-crystalline solid phase, SSZ-13 synthesised by an IZC method starting from FAU had an increased DCC, which points towards the presence of six membered ring paired Al sites.[1] The addition of lithium ions to such an IZC, which is standard procedure to control the Al distribution in a synthesis starting from amorphous sources, was shown to maximize the DCC (Co/Al= ~0.5) of a high silica SSZ-13 zeolite (Si/Al=~35). This was thought to be due to an interplay of kinetic factors, as Li sped up the crystallisation, and thermodynamic factors through stabilisation of the six membered ring paired Al sites.[3]

However, this success in increasing the DCC did not transfer when utilizing a more aluminous starting source (FAU with Si/Al=of 15 instead of 40), and thus a new strategy had to be designed. By interrupting an IZC (starting from a FAU with Si/Al=40) synthesis when the starting source was fully dissolved (after 40 minutes) and removing some of the silica rich liquid, after which the synthesis was left to react to completion, we were able to reduce the Si/Al ratio of the resulting SSZ-13 daughter zeolite to ~25 without a serious reduction in DCC, which was ~0.41. When even more of the liquid phase was removed at the intermediate stopping point, a serious reduction in DCC took place. This technique of intermediate stopping and cooling of an IZC synthesis later on appeared to be even more useful than first thought, possibly unlocking new synthesis pathways towards different topologies and zeolite compositions, as well as providing insights into the mechanisms at play during zeolite crystallization.

1132 - ENGINEERING LEWIS ACIDITY IN MFI AND CHA ZEOLITE CATALYSTS BY ELECTROCHEMICAL RELEASE OF HETEROATOMS DURING SYNTHESIS

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Zeolites are microporous materials that consist of connected silica and alumina tetrahedra. As performance materials in catalysis and separation, they hold levers over millions of tons of products, next to guiding the transition to a circular carbon economy. Introducing tetrahedral heteroatoms other than Al, such as B, Sn, Fe, Zn etc., enhances or modifies their (Lewis) acidity, creating a confined single atom catalyst [1]. These so-called zeotypes (e.g., Sn-BEA or Ti-MFI) and especially stannosilicates, have revolutionized biomass conversion and peroxide oxidations [2, 3].

Zeolite formation depends on both kinetics and thermodynamics, and the prevalence of one over the other can lead to different active site densities and distributions. Unfortunately, obtaining a targeted active site (heteroatom) density is never straightforward and the heteroatom metal content is often too low for zeotypes, yielding suboptimal catalytic performances (molproduct.kgcat-1.h-1). For instance, during the direct zeolite synthesis, isomorphous substitution heavily affects crystallization kinetics, prolonging synthesis time up to a significant degree. On the other hand, post-synthetic modification techniques provide a compromise in time, although their outcome rely exclusively on the properties of the parent material [4].

Here [5], we attain exceptional levels of control over heteroatom incorporation in siliceous zeolites based on introducing conducting metal electrodes in bulk hydrothermal synthesis mixtures. The electrochemical heteroatom release by anodic oxidation can be precisely timed for minimal interference with zeolite nucleation and allows for unique concentration control during the growth phase. Depending on a new reactor design, this novel method provides zeolite synthesis control by additional degrees of freedom expressed in voltage, frequency and electrode surface.

The proof of concept along with essential understanding of the electrochemical concept are demonstrated for Sn-MFI zeolite synthesis, for which, we could reach Si/Sn ratio of 32 at only 90°C. Moreover, by substitution the electrode material to other metals and by changing synthesis environment, we successfully expanded the method towards Al-, Zn-, and the novel mixed metal Sn,Zn-MFI zeolites, as well as Sn-, Ti-CHA. Eventually, the electro-assisted synthesis was proven to be truly generic also in acidic conditions, where Sn-APO-5 (AFI framework) was formed.

Furthermore, the voltage-based feeding of the system with very dilute but active heteroatom precursors allows one to synthesize zeolite catalysts with unprecedented Lewis acid site (LAS) densities. For stannosilicates, we show more than 15-fold increase in the framework Sn content versus syntheses in batch, and in catalytic tests, this leads to materials so rich in active sites that they demonstrate high productivities.

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1146 - EFFECTS OF BINDERS ON THE PERFORMANCE OF MORPHOLOGY HZY HZM 5 ZEOLITES IN HYDROCARBONS TO LIGHT OLEFINS.

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The catalytic cracking of hydrocarbons derived from various feedstocks (fossil fuels, biomass, and plastic waste) provides essential hydrocarbons for the petrochemical industry (ethane, propane, iso/n-butane, and iso/n-pentane). Progress is needed in this field to meet the growing demand for light olefins, which have increased rapidly in recent years [1]. Catalytic cracking is one of the most effective approaches for improving light olefins' conversion, selectivity, and product distribution. The catalyst composition is generally made by mixing a binder and a zeolite in varying proportions to enhance stability, activity and resistance to coking. This study will focus on examining the effect of binders using (kaolin and bentonite) in combination with two commercial zeolites, HZY (Si/Al = 6) and ZSM-5(11.5). Three different weight percentages of ZSM-5 was used in the matrix (5%, 10%, and 20%) with HZY (35%, 30% and 20%) respectively, with a fixed binder composition of 60% {(kaolin (30%) and bentonite (30%)} and these catalysts were incorporated as aqueous slurries.

All catalysts were dried at room temperature and calcined in static air at 550°C (2 °C/min) for 5 h and characterisation measurements (BET, XRD, FTIR, TGA and TPD) were carried out for all catalysts. The catalytic cracking activity of the catalysts was carried out using 2 different feedstocks (n-heptane and n-dodecane) in a quartz reactor tube (ID = 9 mm and OD = 14 mm) at 550°C with N2 as a carrier gas (30-110 ml/min) for varying intervals (5-240 min). The findings shows that the surface area of catalyst particles was reduced compared with commercial zeolites (ZY and ZSM-5) and the binder reduced the overall acidity of the catalysts as they typically makeup 60-75% of the formulated catalyst and can alter the porosity of the matrix due to their amorphous nature.

For n-heptane cracking, the conversion to light olefins for the different catalysts with varying wt% of ZSM-5 is 75-95%, while n-dodecane was from18%- 85% and this can be associated with the degree of pore blockage within the catalyst matrix which is higher in C12 than C7. The light olefins produced were mainly caused by hydrogen transfer via carbenium ion and C–C cracking through the β-scission mechanism during cracking, as reported by S.Matsuura et al. (2021) in their study of hierarchical zeolites in catalytic cracking of n-dodecane [2-3]. Overall, the results indicated that the zeolite catalysts mixed with binders showed preferential selectivity to light olefins(C2-C5) in their product distribution compared with commercial zeolites (ZY and ZSM-5), which tend to give light alkanes.

Increasing the wt% of ZSM-5 in the matrix was also found to provide more light olefins in the product, and this could be related to the shape selectivity and presence of narrower pores that restrict the formation of larger coke-producing molecules. Further work to do adding metals (Ni and Fe) to catalysts.

1153 - ZEOLITE SYNTHESIS FROM NATURAL BAUXITE BY LOW TEMPERATURE VAPOR PHASE TREATMENT

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Bauxites are aluminum deposits formed as results of aluminosilicates rocks weathering under warm, humid, tropical-to-subtropical climate conditions. The chemical and mineralogical composition, mainly characterized by the presence of boehmite and kaolinite, makes these rocks as natural sources of Si and Al and therefore as inexpensive raw materials for the zeolite synthesis. Several patents and literature data have in fact documented the zeolite formation by mixtures of bauxite and kaolinite or waste (e.g. rice husk) [1,2]. Many more papers have documented zeolite synthesis from waste bauxite products (red mud or bauxite tailings) [3].
In this work, three samples of bauxite were used as natural raw material for the zeolite formation by a green process based on vapor-phase crystallization (VPC) method without the addition of pure chemical components or other sources but only exploiting the chemical composition of the natural raw materials. In detail, the synthesis was carried out using a water bath with deionized water heated at 35, 45, 60 or 90 °C. During the process, NaOH pre-fused bauxites were contacted only with vapor from the liquid.
The results display that zeolite formed in all the samples. The data indicate that the $SiO2/Al2O3$ ratio, the competitive presence of geopolymers vs glass in amorphous materials and the general lower amount of water molecules, control the synthesis of zeolite with LTA topology during VPC at low temperature (35 and 45 °C). The larger amount of water by vapor crystallization treatment at higher temperature (60 and 90 °C) determines, instead, the formation of more stable sodalite with typical well-defined rose-like
The zeolite crystallization mechanism at lower temperature takes place essentially through a solid-state transformation process of geopolymers into well-defined crystals whereas the processes at higher temperatures can be approximate to a hydrothermal process improving geopolymers transformation. This is in accordance with literature [4] describing VPC method as an intermediate mechanism between solid-state transformation and hydrothermal synthesis.
Besides the mechanisms determining the type of zeolite crystallization, the results shown in our experiments indicate that the vapor phase crystallization process represents a green and economic method to form zeolite reducing the amount of water and, most important think, generating no liquid waste generally produced by conventional hydrothermal method

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1161 - EXPERIMENTAL AND COMPUTATIONAL MECHANISMS THAT GOVERN LONG TERM STABILITY OF CO2 ADSORBED ZIF 8 BASED POROUS LIQUIDS

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Herein, we present a combined experimental and computational study on MOF based porous liquids (PLs) for CO2 capture and their stability to aging. There is currently an intense scientific search for CO2 capture materials that are effective in industrial and dilute gas streams to limit global warming.[1,2] While aqueous amines are currently use in industrial carbon capture systems, they have considerable challenges in implementation, such as high energy regeneration processes and corrosivity that need to be overcome with either substitute methods or alternative materials.[2-5] This has resulted in expanded research to CO2 capture capabilities in ionic liquids, porous liquids (PLs), and solid adsorbents, such as zeolites and metal–organic frameworks (MOFs).[6-13]

Another obstacle for using solid sorbent materials in industrial CO2 capture is the difficulty in retrofitting current emission sources compared to liquid sorbents. PLs are an active area of materials research to address this challenge. PLs are an emerging sorbent material with properties that take advantage of the permanent and rigid porosity of porous solids and the fluidity of liquids.[13-15] There are four different types of PLs.[16] Type 3 PLs composed of a solid sorbent host suspended in a pore excluded solvent system have garnered attention due to the tunability of the solid-porous hosts (such as MOFs, Zeolites, or porous organic cages) and the solvent system.

The porous host in the PLs studied is solid ZIF-8, a nanoporous framework that is known to degrade when exposed to CO2 in wet environments and therefore the long-term stability of ZIF-8 based PLs is unknown. Through aging experiments, the long-term stability of a ZIF-8 PL formed using a water, ethylene glycol, and 2-methylimidazole solvent system was systematically examined and mechanisms of degradation elucidated. The PL was found to be stable for several weeks with no ZIF framework degradation observed after aging in N2 or air. However, for PLs aged in a CO2 atmosphere, formation of a secondary phase occurred within one day from degradation of the ZIF-8 framework.

Examination of the chemical stability over 13 weeks is correlated with the chemical reactivity of the components when CO2 is adsorbed into the system. This combined formulation and materials characterization study involved PXRD, FTIR spectroscopy, and 13C NMR spectroscopy. Furthermore, computational density functional theory (DFT) calculations were used to predict the preferential reaction mechanisms between CO2 gas and PL components, elucidating the degradation in the PL system with CO2 adsorption.

Through combination of experimental and computational techniques, the chemical factors that control the long-term stability and sensitivity of ZIF-8 based PLs to CO2 were identified to include MOF crystallite size, CO2 aging of solvent to form carbonate species, and MOF degradation due to interactions with the solvent.[17] These long-term studies identify that ZIF-8 PLs formed using aqueous solvent systems are stable in air and inert gases. However, high concentration CO2 exposure leads to changes in the porous ZIF framework as well as in the composition of the solvent system.

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1169 - STABILIZATION EFFECTS OF PORE FILLERS IN POST SYNTHETIC LIQUID MEDIATED MODIFICATION OF ZEOLITES

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The successful application of zeolites in diverse fields largely relies on their high stability compared with other porous materials. However, the property requirements for zeolites have become severe due to their diverse and demanding applications. Aluminosilicate zeolites are utilized for adsorptive and catalytic applications, wherein they are sometimes exposed to high-temperature steaming conditions. Development of extremely stable zeolites that can withstand over 1000 °C steaming was realized by post-synthetic stabilization treatment [1]. High-silica zeolites such as ZSM-5, mordenite, and beta could be stabilized by significantly reducing the defect sites via a liquid-mediated treatment without using additional silylating agents, in which a fluoride anion, hydroxide anion, and pore filler cation were used cooperatively. Zeolite frameworks seems to be reconstructed during the treatment, and pore filler contributed to maintain the frameworks. The same treatment can be applied for defect healing of beads-milled CIT-1, which showed extended catalytic lifetime on methanol-to-olefins reaction [2]. Furthermore, the concept of pore filler stabilization was successfully extended to post-synthetic dealumination of small pore zeolites, and an unexplored scheme named pore-opening migration process (POMP) was proposed [3]. Despite small-pore zeolites are gaining increasing attention owing to their superior catalytic performance, post-synthetic tuning of bulk Si/Al ratios of small-pore zeolites has not been achieved with well-preserved crystallinity because of the limited mass transfer of aluminum species through narrow micropores. Acid treatment assisted by stabilization of the zeolite framework by organic cations in pores is proven to be successful for the removal of Al species from zeolite via POMP. Furthermore, the dealuminated AFX zeolite is treated via defect healing, which yields superior hydrothermal stability against severe steam conditions. The findings could facilitate industrial applications of zeolites via post-synthetic modification of aluminum content and defects, and could elucidate the structural reconstruction and arrangement processes for inorganic microporous materials.

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1172 - A PHOSPHAZENE BASED ROUTE FOR SYNTHESIS OF EXTRA LARGE PORE ZEOLITE UTD 1

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Zeolite UTD-1 was the first silica based extra-large zeolite with pore apertures formed by 14 tetrahedra, opening the possibility of processing large molecules by zeolite-based catalysts.[1] The material has been traditionally prepared by using the organometallic bis(pentamethylcyclopentadienyl)cobalt(III) cation (Cp*2Co+) as Organic Structure-Directing Agent (OSDA), which is expensive and needs of a relatively laborious working up to be obtained in the hydroxide form that is employed in the synthesis. The use of a cheaper OSDA, N,N-dimethyl-(2-methyl)benzimidazolium hydroxide, has been recently reported to synthesize UTD-1 in pure silica and aluminosilicate forms.[2] Phosphorous-based OSDAs have been proven as versatile OSDAs for the preparation of several zeolites.[3] Here, we will describe the use of the phosphazenium cation 1,1,1,3,3,3-Hexakis(dimethylamino)diphosphazenium, as a highly effective OSDA for the synthesis of UTD-1 materials in a wide range of synthesis conditions. Zeolite UTD-1 was typically obtained from synthesis gels having the following chemical composition: (1-x) SiO2 : x Al2O3 (or B2O3) : 0.4 OSDA : 15 H2O, where x was varied from 0 – 0.025 and OSDA was the 1,1,1,3,3,3-Hexakis(dimethylamino)diphosphazenium hydroxide. The gels were heated at 408 K for 7 – 30 days under rotation (60 r.p.m.). The solids were recovered by filtration, washed with distilled water, and dried at 373 K for 12 h. The as-made materials were treated at 973 – 1123 K under a 20% H2 in N2 stream. Zeolite UTD-1 has been obtained as pure silica, borosilicate and aluminosilicate forms by using the phosphazenium cation as OSDA. The maximum incorporation of B and Al into the zeolite UTD-1 by direct synthesis was a molar ratio Si/B up to 40 and Si/Al up to 38. The incorporation of the B and Al atoms in the framework of the zeolite was confirmed by 11B and 27Al MAS NMR spectroscopy, respectively. The OSDA decomposes during the heat treatments under a H2/N2 stream forming P-species that are partially removed out of the solid. The presence of extra-framework P-species interacting with the Al sites modifies the acid properties of the zeolite. The phosphazenium cations showed high stability in alkaline media. Moreover, not only the phosphazenium cation occluded in the channels of the zeolite, but also the cation remaining in the liquid media was stable in the synthesis medium. Upon zeolite crystallization, the UTD-1 crystals were recovered by filtration and the mother liquor was collected and used as OSDA in a second synthesis cycle. Pure high crystalline UTD-1 was the only phase observed in the obtained products. By this method, around 50% more of the zeolite UTD-1 can be obtained by using the same amount of OSDA. Ideally, all the OSDA used in the synthesis could be incorporated into the final zeolite reducing the cost of the process as well as the wastewater amount.

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1175 - DEVELOPING REACTOR BASED SOLUTIONS FOR MONITORING AND CONTROLLING OF ZEOLITE SYNTHESIS

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Zeolites have been widely used in many applications related to industrial catalysis, ion exchange, and adsorption. Despite the unique characteristics that make zeolites a promising choice for myriad chemical processes, their synthesis has some limitations. Throughout the years, researchers have worked to expand the boundaries and major researches have focused on adopting ingredient-based solutions. For instance, Interzeolite conversion and seed-induced synthesis have been employed to shorten synthesis time, Dual OSDA approach [1], [2] is a way to obtain enhanced structures, and novel P-based OSDAs [3] have been used to develop stable catalysts while one of the ideas behind Charge Density Mismatch (CDM) is to force OSDAs with different charges to cooperate or obtain a higher Si/Al ratio. With the exception of the continuous systems developed by the Tokyo group [4], most zeolite synthesis methods rely on batch reactors which do not allow intermediary checking of the synthesis progress without cooling-opening-sampling. On top, once a batch is closed, control along the way is lacking. Nevertheless, monitoring of the physical conditions and true synthesis sampling at temperature and under the autogenous pressure, could help to understand the progress of a synthesis. Here we are developing an active tool that facilitates synthetic fine-control of zeolites to be able to add things along the way and better control the physical environment of the synthesis, including the option to monitor and sample. This will lead to a better understanding of some of the unknown interactions and gradients which sometimes determine the kinetics and outcome of zeolite synthesis.

While, due to the nature of batch reactors these interactions or mid-synthesis concentration changes cannot be accessed directly, the basic idea of “Fed-batch” reactors is to directly impact concentration profiles by a timed and gradual ingredient feeding during synthesis. In addition, thanks to this “Fed-batch” reactor's sampling feature, samples could be extracted at operational temperature and pressure along with the synthesis, giving a more accurate picture of growing structures. In this talk, a short report will be given on controlled zeolite synthesis in Fed-batch reactor by in situ monitoring synthetic parameters like temperature, pressure and pH. Moreover, an efficient way will be described for building S-curves from one synthesis only, with sampling and yield extrapolation. This is shown for different systems (high and low temperature) without interfering. Having a more precise picture of zeolite formation would make a Fed-batch more efficient than conventional batch systems for incorporating heteroatoms. It seems a lot of discoveries could be expected by adopting new reactor designs in the world of zeolites, especially now, when they could help ongoing efforts toward the more carbon circular chemical industry.

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1180 - INTERZEOLITE CONVERSION FOR FAST AND CONTINUOUS ZEOLITE SYNTHESIS

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Current industrial and laboratory zeolite synthesis relies on batch autoclaves, despite their limited process control and poor performance. Such reactors require long heating times in order to achieve synthesis temperature, and show slow diffusion rates of the precursor materials due to insufficient mixing[1]. In addition, hydrothermal synthesis has an intrinsically long crystallization time. Interzeolite conversion has been recently explored as a technique to achieve fast zeolite synthesis, that otherwise would not have been possible through traditional hydrothermal processes[2]. Moreover, moving from batch to continuous synthesis, thermal lag and poor mass transfer can be tackled. Engineering considerations are required to achieve successful transition. It is necessary to take into account the high temperatures and high pressures that are normally required for zeolite synthesis, plus the need of dealing with a concentrated suspension throughout the whole crystallization time. Solid deposition has been successfully prevented in organic crystallization and organic chemistry by the use of ultrasound as an external energy source[3]. Ultrasound also provides intense mixing and a possible alternative pathway to zeolite synthesis, which would make interzeolite conversion even faster[4].

Two systems are investigated for the transition from batch autoclave to fully continuous synthesis: a stainless steel tubular batch reactor (5 mL volume), and a PTFE coiled tubular reactor (10 mL volume).

Interzeolite conversion of USY dealuminated zeolite to MFI has been first tested in a tubular batch reactor with a molar composition of 1SiO2: 0Al: 0.35SDA+: OH-: 0Na+: 12.5H2O. Proper temperature control of the system throughout crystallization process is achieved via heat transfer fluid immersion. Such a system allows complete removal of the thermal lag that usually occurs in a traditional autoclave, by reaching the synthesis temperature of 160 °C within one minute[5]. The development of such a system enables fast screening of the reaction conditions over time. XRD analysis shows complete dissolution of the FAU mother zeolite within the first 5 minutes, and formation of crystalline MFI between 10 and 15 minutes of residence time. However, such a concentrated suspension causes intense solid deposition when tested in the coiled reactor in a continuous process, which is highly detrimental for product yield and reproducibility.

The short residence times give room for dilution of the system (1SiO2: 0Al: 0.35SDA+: OH-: 0Na+: 30H2O), in order to cope with the solid deposition and clogging in the continuous reactor. Introduction of ultrasound to the continuous system can further increase zeolite kinetics and be employed as a tool for clogging prevention. Both silent and sonicated conditions are investigated in the coiled tubular reactor, and crystallinity, reaction time, product morphology, pore size are compared with the traditional batch autoclave and the tubular batch.

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1192 - MICELLES FORMATION INSIDE ZEOLITES A COMBINED 13C NMR AND RAMAN MICROSPECTROSCOPY STUDY

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Hierarchical zeolites have emerged as a solution to the mass transport limitations of microporous zeolites in catalytic reactions involving large molecules. [1] Surfactant-templating is a simple and versatile approach to preparing these hierarchical materials as it preserves the acidity, crystallinity, and hydrothermal stability of the parent zeolite. [2,3] However, up to now, the formation of the micelles inside the zeolite crystals has never been directly observed. Here, by using different techniques, like Nuclear Magnetic Resonance (NMR), Raman Spectroscopy, and Raman microspectroscopy, we were able to observe and follow the homogeneous development of micelles inside individual zeolite crystals. [4] Large NaY zeolite crystals, with a Si/Al ratio of 3.3, were synthesized with an average size of 2 microns, to be able to be monitored by optical microscopy. These large zeolite crystals were treated with a basic solution of the cationic surfactant, cetyltrimethylammonium bromide (CTAB), which resulted in a large amount of well-defined mesoporosity, as observed by N2 adsorption at 77 K. The 13C NMR spectra of the hydrothermally treated sample show broader and shifted resonance peaks as compared to solid CTAB, which is characteristic of a more fluid-like environment similar to a micellar solution of the surfactant. To gain further insights into the distribution and local organization of CTA+ cations, we characterized the CTAB-loaded samples at the single zeolite crystal level using spontaneous Raman microspectroscopy. Whereas these Raman spectra were collected from a location at the center of individual zeolite particles, the presence of CTA+ throughout the whole zeolite was confirmed by spatially mapping the CH-stretching signal at different focal planes with SRS microscopy. The CH region, while complex in nature due to the overlapping CH2 and CH3 symmetric and asymmetric stretching modes, contains valuable information on the organization of CTA+ cations inside the zeolite particles. We were able to link the relative Raman signals intensity of the 2930 cm–1 (symmetric CH3 stretching) and 2850 cm–1 (symmetric CH2 stretching mode) to the local polarity surrounding the CTA+ alkyl chain environment.

By combining 13C NMR and Raman microspectroscopy, we could unequivocally prove that during the hydrothermal treatment steps, the individual CTA+ molecules first penetrate inside the zeolite crystals and then self-assemble to form micelles in the interior of the zeolites. Moreover, with Raman microspectroscopy, we have been able to spatially resolve in 3D the presence of these micelles throughout the zeolite crystals, which confirms our previous observations of the presence of well-defined mesoporosity homogeneously distributed inside the zeolites.

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1193 - CORRESPONDING AUTHOR PATRICIA HORCAJADA (PATRICIA.HORCAJADA@IMDEA.ORG) A FAST AN EASY MICROWAVE RECIPE TO METAL NANOPARTICLES@METAL ORGANIC FRAMEWORKS WITH CATALYTIC HYDROGENATION ACTIVITY

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The search for inexpensive and efficient catalysts, which are easily synthesized, to carry out reactions with industrial interest is under continuous study by the scientific community. Some advantages, such as the availability of the starting reagents, reaction times, high yields, purification and storage, are very interesting topics in order to design a potential catalyst. In this context, metal-organic frameworks (MOFs) are considered great candidates as catalysts due to their remarkable and tuneable properties, such as high surface area, porosity, uniform pore structure, and versatile composition [1]. In this work, we explore MOFs as hosts for the deposition of metal nanoparticles (MNPs) using a fast and easy microwave (MW) approach. Additionally, these composites were tested on challenging hydrogenation reactions: 1) the selective reduction of light olefins into paraffins and, 2) the dehalogenation of chlorinate organic compounds. On this matter, the highly porous and robust zirconium carboxylate MOFs UiO66-NH2 and NU-1000 were obtained by a simple and effective MW-assisted method (85% isolated yield, 30 min) [2]. In addition, the deposition of different MNPs (Ni, Co and Pd) were performed via chemical reduction by MW, optimizing the process to be carried out in aqueous medium, short irradiation times, and relevant quantities (860 mg). The structure, morphology and particle dispersion of the resulting MNPs@MOF composites were characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) and the MNP loading determined by Inductively Coupled Plasma (ICP-OES), reaching composites with tuneable metal content (X=1-5%) and a homogeneous dispersion of small MNPs (~4 nm). Related to the catalytic activity, these MNPs@MOFs were studied for the hydrogenation of light olefins to generate their respective alkane obtaining quantitative conversions after 1 h in really mild conditions (1 bar of H2 pressure, room temperature, and using a "green" solvent such as ethyl acetate). The highest yield towards n-hexane was achieved using the Pd (2.5%)@UiO66-NH2 composite, exhibiting high selectivity (≥99%) to the desired product after 3 cycles. The scope of the reaction was extended to long-chain terminal alkenes and cycloalkanes, getting remarkable results on selectivity and activity. On the other hand, the hydrodehalogenation experiments in vapor phase were performed at 250 ºC, 5 bar of N2+H2 for 2 h, achieving a complete conversion of the organochlorinated compound by Pd@UiO66-NH2 while maintaining the crystal structure of the catalyst as XRD results confirmed.

In summary, our study demonstrates that MNPs@MOF composites, such as Pd@UiO66-NH2 and Pd@NU1000, are potential and easily-to-made materials for different reduction reaction applications. The synthetic approaches that implicate MW heating can be performed successfully to obtain composites in a fast and profitable way and extended to other metals. Finally, these advantageous methodologies to form these materials could lead to rapid and deep development of different catalytic applications.

1195 - ZR BASED METAL–ORGANIC FRAMEWORKS AS CATALYSTS FOR THE ALDOL CONDENSATION OF BIOMASS DERIVED FURFURAL INTO BIO JET FUEL PRECURSORS

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The development of Sustainable Aviation Fuels (SAFs) is expected to play an increasing role for the European Union decarbonisation strategy that requires to achieve the ambitious goal of 63-68 % of total EU jet fuel consumption by 2050. Between different alternatives, the transformation of lignocellulosic biomass into jet fuel-range molecules via chemical conversion appears as one of the most promising [1].
In this contribution, the aldol condensation of furfural, a platform molecule derived from crude lignocellulosic biomass, with ketones has been studied. Most research is focussed on the catalytic aldol condensation of furfural with acetone, obtaining mainly C8 compounds. In order to get components within traditional Jet A1 fuel blending, usually C8-C15 alkanes, larger ketones, as methyl isobutyl ketone (MIBK), must be used. Hence, in this work the aldol condensation between furfural and methyl-isobutyl-ketone (MIBK) to produce the corresponding C11 oxygenated adduct (FuMe), has been studied. By a subsequent step of hydrodeoxygenation (HDO), the precursor FuMe can be transformed into a promising SAF.

We recently reported a Zr-based Metal-Organic-Framework (MOF) as a heterogeneous catalyst for the synthesis of jet fuel precursors through aldol condensation reactions [2]. However, such Zr-MOF evidenced a gradual loss of activity over multiple reaction cycles. Therefore, more active and stable catalysts to transform furfural into jet fuel precursors through aldol condensation should be found.
In this line, we have synthesised catalysts based on different Zr metal–organic frameworks supported onto mesoporous silica following the in-situ synthesis reported by Rojas Buzo et al. [3] and we have tested them in the aldol condensation of furfural and MIBK to bio-jet fuel precursors. Hybrid Zr-MOFs/silica materials exhibit higher condensation activity than the unsupported crystalline Zr-MOFs due to the improvement of the catalyst properties, as confirmed by means of different analytical techniques. On the one hand, the remarkable textural properties of the silica support lead to catalysts with high surface areas and large mesopore volumes. On the other hand, a Zr species surface dispersion is achieved, which confers strong Lewis acidity. In addition to improving the catalytic activity, the hybrid materials have shown greater stability over successive condensation reactions. Therefore, we have shown that this strategy allows to enhance the catalytic production of FuMe in an efficient and highly selective way, with an enhanced stability of the catalyst, a critical challenge when facing the commercialization stage of any catalytic process.

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1196 - IN SITU INVESTIGATION OF ZEOLITE SYNTHESIS WHILE MILLING AT ELEVATED TEMPERATURES

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Mechanochemical reaction is defined as a "chemical reaction that is induced by mechanical energy" by means of compression, shear, or friction. Some previously unknown reactions or believed unlikely were facilitated by mechanochemistry thus offering alternative reactivity and sometimes different product selectivites [1]. Clearly, the milling treatment offers new reaction pathways in the systems with identical initial chemicals as in solutions [2]. Advantages of this synthesis route are markedly reduced use of solvents, time saving, less waste and energy consumed, lower reaction temperatures. Further, starting materials different than in solution systems can be used and the required equipment is rather simple. Mentioned points make mechanochemistry eco-friendly synthesis technique, particularly interesting for industrial application in managing the global problems of pollution, growing energy demand and shortage of raw materials. Plethora of advantageous impacts of the mechanochemical treatment step in zeolite chemistry such as preparation of nanosized crystals and post-synthesis recrystallization was reported [3,4].

Zeolite synthesis is recognized as a "geoinspired" process based on the hydrothermal treatment of Al- and Si-containing precursors in alkaline solutions at reaction temperatures up to 250 ºC, generally conducted in autoclaves placed in ovens [5]. Developing milling processes to attain zeolite materials is deemed as an important issue from environmental, technological but also materials' engineering point of view [4]. This paper provides account that may result in achieving favorable circumstances to perform successful mechanosynthesis of zeolites using soluble and/or amorphous source chemicals. Several zeolite materials (LTA-, MFI-, MOR-, CHA-type) were prepared in Teflon-lined milling jars at 30 Hz grinding frequency and temperature in the range 80 – 150 °C. The syntheses were conducted for up to 3 h. The reactions were followed via in situ synchrotron X-ray diffraction. The compiled data indicate that LTA- and MOR-type materials crystallize readily in less than 1 h, whereas MFI-type zeolite formation took more than 2 h and exhibits rather low crystallinity degree, despite added seeds. Indeed, the results obtained in the scope of this investigation will provide directions for further optimization of mechanochemical treatment of zeolite synthesis mixtures and subsequently enhance the possibilities in fabrication of materials with tailored properties.

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1198 - POROUS MATERIALS FOR HYBRID FUNCTIONAL NANOCOMPOSITES METAL AND ORGANIC NANOWIRES CONFINED IN ZEOLITES AND MESOPOROUS SILICA

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The creation of novel functional materials is a technological need and a scientific challenge for the production of innovative systems able to face the requirements of many application fields. Cooling technologies are useful in many fields related to daily life (domestic refrigeration, computer cooling, air conditioning ...) as well as high technology (cooling of optoelectronic devices, superconducting devices, thermal management of electronic devices ...) In this, all-solid technologies based on the thermoelectric effect such as Peltier cooling devices represent a real alternative, as they have no moving parts, are compact and reliable. Despite the technological advance of the system, large-scale applications of Peltier cooling devices have been limited so far, mainly due to their insufficient performance and their rather high cost. While typically used alloys can be toxic and expensive, Bi1-xSbx alloys have a strong potential for cooling applications. Therefore, the insertion of the metallic component inside of a porous structure, such as zeolite channels and silicas pores, could improve the thermoelectrical properties with respect to the bulk material. One of the systems that are explored is formed by silica nanotubes in which Bi metal is inserted to form nanowires. Among the many parameters, the channel arrangement and dimensionality are of crucial importance in obtaining metal nanowires affecting the outcome performances of the composite. The specific aims are the decrease of thermal conductivity and the increase of the Seebeck coefficient by exploiting the quantum confinement of the metal phase.

Besides metals, also organic molecules are of interest when confined in a zeolite channel. The possibility of insertion and reaction of molecules inside an organized scaffold can lead to new properties of both the inorganic host structure and the organic guest molecule. Exploiting the wide variety of the organic functions, ranging from multiple C-C bonds to the presence of heteroatoms, a multitude of composites can serve to the different purposes of the ever-growing demand of modern efficient materials. In particular, the use of unsatured hydrocarbons monomers allows for the formation of polymers within the porous structure exploring different ranges of temperature and pressures. These hybrid materials are of interest for applications in gas sensing and for green hydrogen generation. Promising systems are the AlPO-54/polyacetylenes systems for which the polymerization of the phenylacetylene and diphenylbutadyne molecules was obtained. The systems are studied and characterized by infrared, Raman and nuclear magnetic resonance spectroscopy, transmission electron microscopy and X-ray neutron diffraction both at ambient pressure and at high pressure to provide a rich description of the host-guest interactions.

1211 - HIGH SILICA (B FE) BEA ZEOLITE SYNTHESIS AND APPLICATION IN HMF ETHERIFICATION

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The beta structure consists of a three-dimensional network of channels with a twelve member rings openings with diameter of 7.6 x 6.4 and 5.5 x 5.5 Å. These characteristics classify beta as large structure zeolite. Beta zeolite was first synthesised in 1967 by Wadlinger et al., [1] by adopting a basic synthesis gel containing tetraethyl ammonium as template, obtaining Al-containing beta zeolite in a wide range of Si/Al molar ratio, i.e. 5-100. The synthesis of beta zeolite with Si/Al in the range 10-30 is common and easily implementable. On the contrary, the synthesis of beta crystals with Si/Al out from this range is more difficult and innovative strategies have to be adopted. During the last decades, zeolite scientific community also focused on isomorphous substitution of Al3+ by trivalent metal atoms, such B, Fe, Ga, with the aim to have a control on the acidity, especially for application in which acid site strength plays a crucial role, as in catalysis [2]. At the best of our knowledge, no studies have been reported on the preparation of Al-free high-silica beta zeolite starting from a synthesis gel containing both boron and iron.

In this study, we report the synthesis procedure and characterisation of Al-free (B,Fe)-beta zeolites prepared with different synthesis gel Si/Fe molar ratio, i.e. 100, 200 and infinite, by using TEAOH as structure directing agent in order to studies the effect of synthesis gel composition on the surface properties, e.g. acidity measured by FT-IR, and on the catalytic performances in the etherification 5-hydroxy-methyl furfural (HMF) with ethanol. Such reaction has an applicative interest in the production of fuel green additives and it is strongly dependent on acid sites types and strength, therefore it can be considered a probe reaction suitable to investigate the role of surface properties of the prepared Al-free (B,Fe)-beta zeolite samples [3]. In this study we focused on the formation of 5-(ethoxymethyl)-furan-2-carbaldeyde (EMF).

Characterization via TG/DTA technique reveals an important effect of heteroatom type on TEA+-zeolite framework interaction and total SDA content per unit cell, while FT-IR measurements carried out by using both pyridine or deuterated acetonitrile as probe molecule indicate that surface acidity, i.e. Brønsted/Lewis/defects, can be tuned by controlling both heteroatom type and amount. Other techniques, such as XRD, N2 adsorption/desorption isotherms, SEM, EDX, NH3-TPD were also carried out for characterization. Catalytic results show that there is a beneficial effect of boron presence on catalysis of HMF etherification and production of EMF. The combination of boron and iron allows to obtain high EMF productivity. In particular, Al-Fe-free B-beta sample exhibits an EMF productivity similar to B-Fe-beta with Si/Fe=100, higher than B-Fe-beta with Si/Fe=200. Kinetic modelling indicates a significant effect of surface acidity and defects on reaction mechanism and selectivity.

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1212 - ONE POT SYNTHESIS OF CHABAZITE WITH HOMOGENOUSLY DISTRIBUTED FE SPECIES USING A NOVEL FE ORGANOMETALLIC TEMPLATE

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Nitrogen oxide (NOX) emissions from industrial processes and transportation continues to cause harm to both the environment and human health through producing acid rain, depleting ozone and causing cardiovascular and respiratory problems in humans.[1] Over the past 50 years selective catalytic reduction of NOX by ammonia (NH3 -SCR) has been successfully used to limit NOx emissions. Iron and copper zeolite catalysts have been extensively used for NH3-SCR due to their high activity, high selectivity to N2 and low N2O formation. While Cu-based zeolites are favoured for NH3-SCR application due to their excellent activity and stability at lower temperatures, Fe-zeolites have shown greater stability at higher temperatures typical of diesel exhausts and lower N2O formation.[2] Improving the lower temperature activity of Fe-Zeolites is of great interest to industry. It is generally accepted that most Fe species such as isolated Fe2+, Fe3+ and FexOy oligomers can contribute to the NH3-SCR reaction while highly aggregated iron oxide has been shown to favour ammonia oxidation side reaction.[3] Isolated Fe species have been found to be the major low-temperature active sites in NH3-SCR.[4] Considering this, it would be advantageous to synthesize Fe-Zeolites with a high proportion of isolated species while inhibiting larger iron oxide particles. Controlling the species of Fe within zeolite is difficult due oxidation of Fe and the various forms Fe can adopt in aqueous solutions, one-pot Fe introduction methods can overcome these issues and stabilise the Fe species.

Ferrocene is an iron containing organometallic compound consisting of two cyclopentadienyl rings bound to a central Fe atom in a 2+ oxidation state. Ferrocene is very stable in air, water, in strongly basic conditions and at high temperatures up to 400 °C. Ferrocene can also be modified to include trimethyl ammonium functionality and has a similar size to that of a cha cage. With all these features in mind it makes it a good candidate as a structure directing agent in chabazite synthesis. Once the chabazite is formed, calcining the zeolite with the ferrocene template intact is expected to lead to the formation of isolated Fe species within the zeolite.

In this work we have used (Ferrocenylmethyl)trimethylammonium hydroxide (FMTMA OH) as a template in a one-pot method to produce homogenously distributed Fe species in chabazite. To the best of our knowledge this is the first example of using FMTMA OH as a structure directing agent in the synthesis of Fe chabazite. We present the extensive work that was undertaken to find suitable conditions for this synthesis, including understanding properties of FMTMA OH and how best use in zeolite synthesis and, additionally, understanding how the calcination conditions affects the Fe species in the final material. This zeolite was also tested fresh and aged under standard NH3-SCR conditions and compared to conventional incipient wetness impregnated samples. Our fresh material showed good comparable conversion to the benchmark, yet the aged material showed greater deactivation compared to the benchmark. Analysis of the aged samples showed very little change in the Fe distributions in the chabazite made using FMTMA OH, while significate re-dispersion was seen in the aged incipient wetness sample. We hope this work will further the knowledge in identifying the active species in low and high temperature Fe-zeolite catalysed NH3-SCR.

1216 - CATALYTIC ACTIVATION OF N2O AND CH4 OVER METAL EXCHANGED ZEOLITES

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Fe-containing zeolite catalysts with redox function have attracted considerable attention for their stabilization of the α-Fe/α-O sites, which are well-known as the active sites for the partial oxidation of methane to methanol [1], benzene to phenol [2, 3], and selective catalytic reduction (SCR) of NOX [4] and catalytic N2O decomposition [5]. The preparation of Fe-containing zeolite catalysts involves post- and direct-synthesis methods [4]. The post-synthesis route has the advantage of adjusting iron content at will, however, the iron species are easily aggreged and not in ideal condition. On the contrary, the direct way can help to embed Fe ions into the framework. After calcination, thus embedded Fe ions in the framework are prone to migrate to the extra framework at the dispersed cationic position [4], which was thought as the active center for reactions such as C-H activation and NH3-SCR. Among various zeolites, Fe-zeolites with small pores have been reported to be more active in the conversion of methane to methanol compared to Fe-zeolites with large- or medium-por.
AEI-type aluminosilicate zeolite, i.e. SSZ-39, with three-dimensional 8R pore and medium size cages that can include spheres up to 7.3 Å, has exhibited splendid catalytic competence in the NH3-SCR and the methanol to olefins (MTO) reactions, which is regarded as an extremely promising small-pore zeolite. Hence, the direct synthesis of Fe-AEI zeolites through one-pot synthesis methods has strongly been desired, not only to avoid the post-synthetic cation exchange procedures under controlled atmospheres but also to allow a better metal distribution and stabilization within the zeolitic crystals. Although the direct preparation for Fe-containing AEI zeolite, the synthesis conditions have not been fully investigated [6].

Herein, Fe-containing AEI-type aluminosilicate zeolites (Fe-AEI) with varied Si/Fe ratios were successfully one-pot synthesized by the interzeolite conversion (IZC) method using the FER-type zeolite in the presence of additional Fe source. The states of Fe species and the acidity of the Fe-AEI zeolites were carefully identified. These Fe-AEI zeolites demonstrated excellent performance in the MeOH formation rate and N2O decomposition at 350 oC, which was much better than the ion-exchanged Fe/AEI zeolite catalyst with the similar Fe content. We have claimed that the high MeOH production was ascribed to the active α-Fe, and the high N2O decomposition was due to both the active α-Fe and the presence of methane. Moreover, the influence of reaction conditions were systematically investigated. For high methanol selectivity, the reaction was conducted at 250 oC and the highest ca.11 µmol.g-1.min-1 MeOH formation rate with 75% selectivity was obtained. For the high N2O conversion, the reaction was carried out at 350 oC and the highest MeOH formation rate of ca. 57 µmol.g-1.min-1 with ca. 99% N2O conversion was obtained. Direct conversion of methane using N2O as the oxidant on the one-pot synthesized Fe-AEI zeolites bring out high methanol formation rate and ultra-high N2O conversion, which greatly addressed both energy and environmental concerns.

1217 - TUNING THE ALUMINUM DISTRIBUTION AND ACIDITY OF ZSM 5 ZEOLITES USING THE MINERALIZING AGENTS DURING SYNTHESES

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Intensive research on improving the catalytic properties of zeolites is focused on modulating their acidity and the distribution of associated Al sites. Owing to the crucial role of acidity in heterogeneous catalysis, much effort is devoted to control the reactivity and selectivity of zeolites through the variation of Brønsted acid sites distribution [1]. During zeolite formation, the interplay between negative and positive charges in the growing framework has a considerable effect on the zeolite phase selectivity and stability. The charge distribution, and the related electrostatic interactions, are expected to determine the distribution of negatively charged aluminum tetrahedra in the frameworks of zeolites. These charges are brought by (i) the forming elements sources (Si, Al), (ii) the organic or inorganic cations acting as structure directing agents (SDAs), and (iii) the mineralizing agents (F- or OH-).
An alternative strategy, not yet developed, is to exploit the mineralizing agents as a possible mean to tune Brønsted acid sites distribution. When the amount of negatively charged Al tetrahedra in the zeolite is below that of the positive charges brought by the SDAs, the electrical neutrality is insured by negative charges coming from the mineralizing agents employed. It has been observed that using F- anions as mineralizing agents and varying the Si/Al molar ratio affect the Al sites distribution of ZSM-5 [2]. However, this behavior remained unexplained.

Herein [3], by studying a series of ZSM-5 zeolites over a broad range of Al content, we demonstrate how the nature of the mineralizing agent (F- or OH-) used in hydrothermal syntheses directly impacts Al sites distribution. The proportions of Al sites, probed by 27Al NMR, depend on the Si/Al ratio for F-, but remain identical for OH- (from Si/Al=30 to 760). This leads to contrasting variations in weak and strong acidities that was also observed with NH3-TPD. Such opposite effect of mineralizers is explained by the spatial location of negative charges and the resulting balance between short- and long-range electrostatic interactions. Preferential Al siting positions can be defined by strong short-range interactions between negatively charged framework areas and positively charged OSDA. This determines a distribution of Al sites that is identical at Si/Al close to 23 (one Al per OSDA) whatever the mineralizing anions. For higher Si/Al values, the other negative compensating charges might tune (F-) or not (silanolates) the Al distribution. Our conclusion is supported by new solid-state NMR data obtained at various magnetic fields (up 20.0 T) and MAS frequencies (up to 100 kHz). This understanding paves the way for additional and simple opportunities to control zeolites' acidity.

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1218 - SYNTHESIS OF CARBOXYLPHOSPHONATE MOFS AND EXPLORING THEIR POTENTIAL IN CO2RR

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Conversion of CO2 into fuel and feedstock chemicals is one of the most promising approaches to achieving net-zero carbon emission. CO2 as a greenhouse gas has been associated with global climate change which is the root cause of various environmental disasters ravaging the world in recent time11. There is an urgent need to revolutionize sustainable conversion technology capable of mitigating the environmental effect of CO2 emission. In recent years, metal-organic frameworks have become a critical material for catalyzing CO2 reduction reactions. The growing interest in the application of Metal-organic frameworks (MOFs) as electrocatalysts in CO2 reduction have been attributed to their excellent catalytic properties22. In recent years, the use of phosphonate ligand with additional carboxylate functional group has found more relevance in metal organic framework synthesis, as the carboxylate functional group can easily coordinate to metal than phosphonate counterpart and can supply additional oxygen atoms to participate in linking to metal ions, which can provide more opportunities to form novel structures3.

In this work, carboxylphosphonic acid was used as ligands to synthesize some MOFs and their catalytic activities toward CO2 reduction reaction were explored. Firstly, the ion exchangeable properties of BIRM-1 were harnessed to incorporate Nickel into its frameworks. Powder X-ray diffraction (PXRD) and scanning electron microscope (SEM) results showed that the crystallinity and shape of BIRM-1 crystals were preserved after Ni2+ incorporation. Also, the SC-XRD data revealed that the crystallographic properties of BIRM-1 matched that of Ni-BIRM-1. However, Ni-BIRM-1 showed poor catalytic activities toward CO2 reduction. Secondly, the CO2 reduction activities of another 2D Nickel MOF was also explored, showing a promising catalytic activity, and producing syngas at 95% faradaic efficiency. A new porous 3D zinc MOF with mordenite zeolite net was synthesized by solvothermal reaction of Zn(NO3)2·3H2O and 4-phosphonobenzoic acid in N, N-dimethylformamide (DMF). This material has been denoted BIRM-13 and possesses the formula Zn2(O3PC6H4COO)2. (DMF).2(DMA).4(H2O). Based on single crystal XRD measurement, this structure exhibits a monoclinic crystal system with a P21/c space group and its asymmetric unit comprises of zinc atom, two deprotonated 4-cpp3− ligands, and three water molecules. One guest water molecule, one DMF, and two DMA molecules were also part of the asymmetric unit. The alternating corner-sharing O3PC and ZnO4 tetrahedrons in compound 2 form a zigzag chain which is bridged by 4-cpp to generate a new 3D zeolite-like open framework.

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1219 - CHEMICAL RECYCLING OF POLYOLEFINS USING NICKEL BI FUNCTIONAL CATALYST VIA HYDROCRACKING A SINGLE SOURCE PRECURSOR APPROACH

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Plastics and their formulated products which have become very important materials in our current society due to their inherent properties (cheap price, light weight, usefulness and durability) are also raising global concern due to their persistence in the environment leading to accumulation in our natural environments as oceans and land with associated ecological implications [1-3]. For example, polypropylene is a major component of single-use facemasks that was widely used in billions during the COVID-19 pandemic. With increasing global polymer production there has been an accumulation of plastic wastes in the environment which requires a route to close the loop and establish a circular economy if we are to target Net Zero by 2050. Hydrocracking, which is a promising alternative to pyrolysis of plastic waste with the use of a bifunctional catalyst, provides a platform to transform plastic waste into useful chemical feedstocks. Here the acidic function is provided by a zeolite support for cracking and hydrogen transfer provided by hydrogenating metals such as platinum and palladium [4]. Due to the high cost and scarcity of noble metals, nickel has been targeted as a substitute metal.

Sulfided nickel, an established hydrocracking and hydrotreating catalyst for hydrocarbon refining, was synthesized on porous aluminosilicate supports for the hydrocracking of polypropylene (PP) and low-density polyethylene (LDPE). Zeolite Beta, Zeolite Y and SBA-15 (an amorphous silica-alumina support) were all impregnated with the single-source precursor (SSP) nickel (II) ethyl xanthate for catalyst support screening using 1-10 wt% Ni loadings. Non-sulfided Ni (1-10%) and 1% Pt loading on the different supports were also synthesiszed using wet impreganation to compare with the sulfided nickel catalysts. All catalyst support were dried at room temperature and calcined in static air at 500 °C (2 °C/min) for 5 h. Prior to hydrocracking, the impregnated catalysts were reduced in H2 or He flow (50 cm3 min-1) at 380, 480 and 500 °C (10 oC min-1) for 10 hrs and characterised using N2 adsorption (BET), XRD, FTIR, TGA and TPD. Polymer hydrocracking was carried out in a stainless-steel Parr anchor stirrer batch reactor (300mL) where the activated catalyst was mixed with polymer pellets in a 10: 1 ratio. All reactions were carried out at 330 oC, for 60-90 minutes with a starting pressure of H2 (20 barg).

SSP-derived 5wt%Ni@Beta yielded a greater than 95 wt% conversion of a mixed polyolefin feed to fluid products and conversion varied depending on the loading of Ni. Liquid and gas products were quantitatively analysed by gas chromatography–flame ionization detection (GC-FID) and gas chromatography–mass spectrometry (GC-MS), revealing a strong selectivity to saturated C4 (37.3 wt%), C5 (21.6 wt%) and C6 (12.8 wt%) hydrocarbons in the case of the SSP-derived catalyst with an i-C4/n-C4 ratio = 2.5, while, the unsulfided Ni-Beta, gave a high yield of methane (C1). Coke levels in the used catalyst ranged from 3-18% and further research on optimized operating conditions of this catalyst can minimize the formation of coke precursors and coke in the micropores of the zeolite and on the surface of both the support and the supported metal. Due to the diversity of polymers, additives and other types of waste (e.g. food, agricultural) that could contaminate even relatively pure polyolefin waste streams, this is an important consideration for advancing the technology readiness level of any chemical recycling technology for polymers beyond uncatalyzed pyrolysis.

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1228 - SYNTHESIS STRUCTURE DETERMINATION AND ADSORPTION PROPERTIES OF THE ZEOLITIC GERMANOSILICATE ITQ 69

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Zeolites are inorganic microporous crystalline materials that present well defined channel systems of molecular dimensions. This characteristic make them useful materials in multiple applications, such as ion-exchange, adsorption, separation and catalytic processes [1]. The search for new zeolites allows to expand their range of applications. In order to obtain novel materials, the development of different organic structure directing agents (OSDA) is one of the most commonly used approaches [2]. Other possibility consists of incorporating heteroatoms different of Si and Al in the zeolitic structure. In particular, germanium has proved to be very useful, as its larger atomic radius introduces some flexibility to the framework [3]. This allows the formation of small units, specially the double four ring cages (D4R), resulting in the formation of structures with very low framework densities.

In this work, the synthesis and structure determination of the new zeolite ITQ-69 is presented, as well as its behaviour as selective adsorbent for industrially relevant light hydrocarbons separations [4].

The synthesis of zeolite ITQ-69 was carried out from gels of different Si/Ge ratio either in fluoride and in basic medium using the organic dication 2,5,5,3a,3b-tetramethyloctahydropyrrolo[3,4]pyrrole-2,5-diium as OSDA. The zeolite was fully characterized, including single crystal analyses (SCXRD). Adsorption isotherms and kinetics of C3 and C4 hydrocarbons were measured in a gravimetric analyser.

The zeolite ITQ-69 samples exhibit XRD patterns that are not coincident with any zeolite structure reported before. The OSDA can be removed by calcination under dry air and the material retains its structural integrity, although it shows clear distortions. The N2 isotherm of the calcined material at 77 K reveals a BET area of 248 m2g-1 and t-plot micropore volume of 0.09 cm3g-1. If these values were recalculated for the hypothetical pure silica material, BET area of 356 m2g-1 and micropore volume of 0.13 cm3g-1 would result, indicating a good microporosity.

Electron microscopy shows the presence of large crystals, especially in the Ge-richest samples, suitable for SCXRD. The analysis of a crystal of pure germania composition indicates that ITQ-69 presents a triclinic structure, with a P-1 symmetry, and cell parameters a=9.2252(2) Å, b= 9.2383(2) Å, c=9.9724(2) Å, α=87.159(1)°, β=65.126(1)°, γ=88.309(1)°, and V=770.08(3) Å3. The structure presents a tridirectional system of interconnected straight small pore channels (8 x 8 x 8R) with elliptical apertures. Taking benefit of the tridirectional small pore channel system, adsorption experiments involving propane/propylene and butane/butenes hydrocarbons were carried out. The results show that ITQ-69 is a promising candidate for the kinetic separation of propylene from propane, as the diffusion of the former is several orders of magnitude faster than that of propane. In the case of butane/butenes, trans-2-butene is adsorbed much faster than other C4 hydrocarbons, but the overall adsorption rates are too low for considering it suitable for this separation.

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1250 - PARTIAL INTERZEOLITE TRANSFORMATION FOR THE FABRICATION OF SUPERIOR CATALYSTS FOR THE CONVERSION OF BULKY MOLECULES

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Interzeolite transformation has been used to produce a novel family of hierarchical catalysts featuring excellent textural properties, strong acidity, and superior catalytic performance for the Friedel−Crafts alkylation of indole with benzhydrol, the Claisen−Schmidt condensation of benzaldehyde and hydroxyacetophenone, and the cracking of polystyrene [1]. Intermediate solids of the FAU interzeolite transformation into BEA display both increased accessibility due to the development of mesoporosity and strong acidity caused by the presence of ultrasmall crystals or zeolitic fragments in their structure. [2]

During the presentation, I will describe a new strategy for the synthesis of superior hierarchical catalysts, whose properties evolve during interzeolite transformation. They are composed of zeolitic fragments and display improved accessibility. Because of these features, they effectively catalyze reactions involving large molecules. We realized this strategy for the interconversion of FAU into BEA. Additionally, we used quaternary ammonium surfactants to develop well-defined mesoporosity in the intermediates. By stopping the interconversion of FAU into BEA at different times, we were able to produce Interzeolite Transformation Intermediates (ITIs) showing optimized catalytic performance.

An important advantage of this strategy is that the physicochemical properties and, therefore the catalytic performance of the hierarchical catalysts can be finely tuned by simply stopping the interzeolite transformation at different times. This creates countless opportunities for the development of hierarchical catalysts [3] with optimized properties and superior catalytic performance for those reactions in which zeolites present significant diffusion limitations.

Additionally, I will present a new approach we have developed for the fabrication of superior catalytic materials made out of building units from different zeolite structures by partial interzeolite conversion using a long chain quaternary amine, which acts both as a structure directing agent (SDA) and porogen (surfactant). This method allows to control the amount of the different zeolitic building units in the final material and consequently to optimize its catalytic performance. We realized this for the cracking of 1,3,5-triisopropylbenzene. Hybrid zeolites yielded a five-hold increase to the desired product at constant conversion over the commercial USY, CBV780, and a 7-fold increase in the conversion of this bulky molecule at constant selectivity over the MFI zeolite

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1259 - ADVANCES IN ZEOLITE TEMPLATED CARBON SYNTHESIS INVESTIGATING THE EFFECT OF TEMPERATURE AND ZEOLITE ACIDITY

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Zeolite-Templated Carbons (ZTCs) are materials that possess exceptional electrical conductivity and surface area due to their microporous and nanostructured nature. As a result, they are well-suited for their use as efficient electrocatalysts and adsorbents in gas storage. The properties of ZTCs make them hence highly sought for various applications such as energy storage, gas separation, and catalysis [1].

The synthesis of Zeolite-Templated Carbons (ZTCs) involves the use of a zeolite as sacrificial template and a carbon precursor, such as ethylene, which can diffuse through the micropore system. Despite some aspects of ZTC synthesis being studied, the influence of the temperature used during the process on the materials properties has yet to be fully understood [2]. In the present study, we examine how the synthesis temperature affects the properties of ZTCs using both a purely siliceous beta zeolite and a protonic beta zeolite (Si/Al = 12.9) as templates.

We have found that when using a purely siliceous beta zeolite, the conversion of ethylene did not occur until a temperature of 700 °C. At this temperature and above, the conversion of ethylene was observed, resulting in the formation of turbostratified carbon on the surface of the zeolite. By contrast, using a protonic beta zeolite allowed for conversion at a much lower temperature; i.e. at 490 °C, resulting in the development of ZTCs. Here, the conversion of ethylene was catalyzed by the acidity of the zeolite. Additionally, when temperatures were increased, thermal decomposition of ethylene occurred as a secondary reaction, leading to the formation of ZTCs with lower quality textural properties.

Our findings indicate that two ethylene transformation paths must be considered: (1) temperature-induced carbon formation and (2) zeolite acid sites-induced carbon formation. For acidic zeolites, ZTC formation was solely induced by acid catalysis at temperatures up to 690 °C. At 790 °C, temperature-induced carbon formation occurred as a side reaction, resulting in the formation of turbostratic carbon, which negatively impact the textural properties of the ZTC. At low temperatures (490 °C), carbonaceous species partially developed in the zeolite template but the formation of well-structured ZTC did not occur probably due to insufficient reactivity at this temperature.

In conclusion, this study provides insight into the impact of synthesis temperature on the textural and chemical properties of ZTCs. The results indicate that the use of protonic beta zeolites allows for the synthesis of high-quality ZTCs at lower temperatures and that the acidity of the zeolite plays a crucial role in the formation of these materials.

1278 - SUPERFAST SYNTHESIS OF CARBON XEROGELS

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The synthesis of resorcinol and formaldehyde to an organic gel proposed by Pekala provides an opportunity to tailor the pore and particle sizes of porous polymers by the variation of pH and dilution of the reaction solution.1,2 Via successive pyrolysis, the porous polymers can be converted to conductive and high surface area carbon xerogels (CXs). Due to the adaptability of the material properties, CXs are promising materials for electrochemical energy storage, as catalysis supports, or as adsorbents.3, 4, 5 However, the production of CXs on a larger scale presents challenges because of the high cost of resorcinol and long and elaborate synthesis processes usually requiring several days.6 This work reports a scalable and facile synthesis route for CXs with specific surface areas ranging from 600 – 700 m2·g-1 (BET) within 5 hours.

The organic precursors were synthesised in a sol-gel reaction with resorcinol and formaldehyde (molar ratio 1:2) with the use of a basic catalyst and water as solvent. After solvation, the sol was prepared via three different synthesis pathways: for the first one (NORM) the gelation proceeded in an oven for two days at 50 – 85°C. As the second pathway, the organic gels were obtained hydrothermally (HT). The resulting wet gels then were dried at elevated temperature and finally pyrolysed. For the superfast synthesis (SF), as the third pathway, the gelation was performed similarly but the drying step was skipped prior to pyrolysis.

For the analysis of the CXs resulting from the three different pathways, N2 sorption, SAXS, TEM and Raman spectroscopy data were recorded. N2 sorption analysis showed that the CXs obtained by the HT route have higher values in SBET, SExt and VPore than the CXs obtained by the NORM route. Furthermore, the porous properties of the CXs from the SF route did not significantly differ from the CXs resulting from the HT route. Regarding the primary particle sizes, SAXS analysis showed that RG of the CXs vary in a range of 76-80 Å. TEM pictures confirmed uniform particle sizes and shape. In summary, the suggested superfast synthesis provides Carbon Xerogels with high surface area and pore volume within 5 hours. Furthermore, the synthesis parameters of the superfast synthesis can be adjusted systematically, allowing tailoring of pore volume, pore sizes, and particle sizes.

1282 - COPPER NANOPARTICLES SUPPORTED ON ZIF 8 COMPARISON OF TWO CU2+ REDUCTION PROCESSES AND APPLICATION AS ALCOHOL OXIDATION CATALYSTS

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Copper-based catalysts are of high potential interest among transition metal for the development of economic and sustainable oxidation catalytic systems. They afford promising alternative to the classic oxidation methods using stoichiometric quantities of toxic inorganic oxidants, such as manganese dioxide, chromium (VI), the Swern or Dess-Martin reagents and to more virtuous but still highly expensive catalytic systems based on the use of precious metals, such as gold and platinum. Herein, we report the synthesis of an efficient and stable heterogeneous catalyst based on copper nanoparticles supported on ZIF-8 for the oxidation of benzyl alcohol under mild temperature and using air as sustainable oxygen source.

After ZIF-8 impregnation with the Cu2+ precursor, two procedures for the reduction of Cu2+ into Cu0 nanoparticles were carried out. On one hand, the copper impregnated ZIF-8 reduction was achieved by soaking the solid in a solution of NaBH4. Alternatively, the solid was submitted to a flow of pure gaseous H2 at 340°C. Physicochemical properties of both Cu/ZIF-8 materials after reduction process were then characterized and compared. The reduction with NaBH4 led to the formation of 15-20 nm sized Cu0 nanoparticles (NP) mainly localized on the external surface of the ZIF-8 crystals. ZnO nanocrystallites were also observed besides the Cu0 nanoparticles, revealing the deleterious effect of NaBH4 on the ZIF-8 integrity, which was not reported so far, to our knowledge. On the contrary, the reduction under H2 flow results in Cu0 nanoparticles with a mean size of 20 nm entrapped within the bulk of ZIF-8 crystals. The location of metal nanoparticles, either on the external surface or within the bulk of ZIF-8 was confirmed by the correspondence of high-resolution transmission electron microscopy (HRTEM) analyses, X-ray photoelectron spectroscopy (XPS) and the comparison of the alcohol oxidation kinetic profiles achieved with the two types of catalyst.

The partial oxidation of the nanoparticles surface of both types of Cu/ZIF-8 catalysts occurs during the storage of the catalysts under ambient conditions, as revealed by high-resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS) analyses. Thanks to the occurrence of these Cu2+ surface species, both types of catalysts were found to be active towards the aerobic oxidation of benzyl alcohol under mild temperature and using air as sustainable O2 source and a nitroxyl co-catalyst as co-catalyst[1]. Benzaldehyde yields of 65% and 60% were obtained with the catalysts reduced with H2 and NaBH4, respectively, at T = 60°C, with a selectivity higher than 95%.

Importantly, the Cu/ZIF-8 catalyst prepared under H2 flow was found particularly stable. Indeed, it could be recycled 5 times without loss of activity, unlike the catalysts synthesized with NaBH4, whose unprotected copper species are exposed on the external surface of the ZIF-8 crystals, leach over the consecutive catalytic cycles. This result demonstrates the critical role of the metal cation reduction process on the performance of the catalysts.

Finally, the most stable catalyst was successfully implemented in a tandem “one-pot” catalytic system associating benzyl alcohol oxidation and Knoevenagel condensation to synthesize benzylidene malononitrile. A yield of benzylidene malononitrile equal to 65 % was obtained based on the benzyl alcohol initial amount, after 28h at T = 70°C.

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1283 - SYNTHESIS OF YFI TYPE ZEOLITES AND INTRODUCTION OF HIERARCHICAL STRUCTURE AND FRAMEWORK TI FOR CATALYTIC APPLICATIONS

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The novel zeolite [Al]-YNU-5 with YFI framework has been first synthesized in 2017 by our research group.1) As a large pore zeolite, [Al]-YNU-5 is expected to improve the diffusivity of molecules by introducing mesopores.2) In this work, we successfully synthesized hierarchical titanosilicate denoted as [Ti]-YNU-5_h by continuous post-synthesis treatments. The [Ti]-YNU-5_h showed excellent catalytic performance for the epoxidation of cycloalkene using H_2O_2 as an oxidant.

[Al]-YNU-5 was hydrothermally synthesized according to the known method.3) As-synthesized sample was calcined at 550ºC for 6 h to remove the structure-directing agent. To obtain hierarchical [Al]-YNU-5 catalyst (denoted as [Al]-YNU-5_h), the calcined sample was desilicated by alkali treatment, followed by appropriate acid-treatments. To obtain [Ti]-YNU-5_h, the [Al]-YNU-5_h was deeply dealuminated by further acid-treatments, and then treated with vapor-phase $TiCl_4$ for incorporating Ti into framework, which was thermally treated at 650ºC for 6 h. Separately, [Ti]-YNU-5 without hierarchical structure was obtained by omitting only the alkali treatment in the above method. TS-1 and [Ti]-MCM-68 were used for comparison. Epoxidation reaction was carried out by stirring 30 wt% H_2O_2(aq), catalyst, solvent (MeCN), and cycloalkene in a pressure tube at 60 ºC for 120 min. The reaction mixture was analysed by GC (FID).
Powder XRD revealed that all prepared samples retained the YFI framework structure. N_2 adsorption–desorption measurements showed significant hysteresis loops suggesting the presence of mesopores within a certain range in [Ti]-YNU-5_h, meanwhile obtained type-II isotherms indicated micropores were intact. Furthermore, in the DR UV-vis spectrum, a peak attributed to the tetra-coordinated $Ti(OSi)_4$ species of the closed site was observed near 210 nm. The epoxidation of cyclohexene and cyclooctene was performed. Compared with the non-hierarchical [Ti]-YNU-5 and conventional titanosilicates, the use of [Ti]-YNU-5_h catalyst gave the desired epoxide products in obviously higher yields. Introducing mesopores through desilication by alkaline treatment may have improved the diffusion of substrates from the liquid phase to the Ti active sites in the micropores of the YFI-type titanosilicate.

1293 - MECHANOCHEMICAL ROUTE FOR SYNTHESIS OF FE SUBSTITUTED ZEOLITES WITH WELL DISPERSED FRAMEWORK FE SPECIES

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Zeolites are crystalline porous materials that exhibit shape-selectivity for various molecules due to their microporous structure [1,2]. Among various applications of zeolites, the catalytic application in the petrochemical field is one of the important roles. Brønsted acidity is the main catalysis of the zeolites, which originates from the bridging OH groups between the framework Si4+ and isomorphously substituted trivalent heteroatoms such as B3+, Al3+, Fe3+ and Ga3+. In addition, the acid strength strongly depends on the kind of heteroatoms. Therefore, the isomorphous substitution of the framework Si4+ atoms with other trivalent cations is an effective approach to controlling the acid property of zeolite catalysts [3].

Yamamoto and Muramatsu et al. have previously reported the mechanochemical method as a powerful synthetic procedure for the incorporation of heteroatoms into zeolite frameworks with various topologies [3,4]. This process proceeds via a mechanochemical reaction followed by a hydrothermal treatment. First, SiO2 and a metal oxide or hydroxide as a source of heteroatoms are mechanochemically reacted by planetary ball-milling to obtain an amorphous Si-metal composite oxide. The thus-prepared composite is then hydrothermally converted into zeolites with heteroatoms in the frameworks. This mechanochemically assisted procedure yields a more homogeneous distribution of substituting heteroatoms in the zeolite framework, compared to the conventional hydrothermal synthesis [3].

Using our aforementioned synthesis strategy, we synthesized the Fe-containing zeolites with various zeolite topologies such as MFI-, MWW- and CHA-type frameworks [5,6]. In this study, the textural properties of the thus-prepared Fe-containing zeolites and their catalytic performance were examined and compared with those zeolites prepared via conventional hydrothermal synthesis in order to clarify the effects of the preparation method. Moreover, we applied the mechanochemical method for the synthesis of Al and Fe-containing MFI-type zeolites, where an excellent catalytic performance was observed in the dimethyl ether to olefins reaction.

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1312 - NITROGEN SURFACE MODIFICATIONS FOR INCREASED INTERACTIONS BETWEEN METAL CLUSTERS AND SURFACE OF 3D GRAPHENE LIKE ZEOLITE TEMPLATED CARBON

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The interaction of metal clusters with a catalysts support modulate the electronic properties of metal catalysts. The electronic interaction between carbon supports and a noble metal is typically weak because of the chemical inertness of the carbon surface basal plane. Consequently, the carbon materials with inert characteristics do not provide strong metal–support interactions. Functionalization of 3D graphene-like zeolite-templated carbon materials with nitrogen heteroatoms was used in this study to form surface nitrogen-containing functional groups and defective centers. The modulation of the metal–metal coordination in 3D graphene-like zeolite-templated carbon materials provided opportunities for tuning the catalytic activity/selectivity/stability. The beta (*BEA) and faujasite (FAU) zeolites in the H+ form of the molecular Si/Al ratios 4 - 12 were used as hard templates for the preparation of 3D graphene-like microporous carbons (β-(N)carbon and Y-(N)carbon). Carbonization of the zeolites was performed using chemical vapour deposition with an appropriate carbon and nitrogen precursors. The pyridinic and pyrrolic groups were incorporated using pyrrole as a nitrogen precursor. Graphitic nitrogen was incorporated using acetonitrile as a carbon and nitrogen precursor. Typical procedure for carbonization employs a diluted stream of the carbon and nitrogen precursor at 700 - 800 °C and aromatization in a stream of nitrogen at 900 °C. The zeolite was removed from the carbon/zeolite composite by leaching using a large excess of aqueous solutions of hydrofluoric and hydrochloric acids. Metal clusters (Pt and Pd) were introduced into the carbon materials using impregnation with organic solutions of corresponding element salt in hexane or acetylacetone as solvents. The effects of increased interaction with the support and reduced metal–metal coordination on activity, selectivity and stability were evaluated in hydrogenation of 1,3-butadiene, 1-hexyne and benzene as model compounds. Activity and stability were compared with the conventional metal supported catalysts. The approach enabled an adaption of the electronic properties and the dispersity of active metal clusters on the carbon catalysts to increase the reaction rates and to tailor the catalyst activity/selectivity/stability.

1333 - SIMULTANEOUS MESOPORIZATION AND METAL INCORPORATION OFFERS SYNTHETIC AND CATALYTIC BENEFITS

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In many zeolite-based catalytic applications, a metal function is included to yield optimal performance. For example, in hydroprocessing reactions, such as cracking and isomerization dewaxing, nickel is deposited on the catalyst to provide the required hydrogenation function. In other cases, a specific interaction with the to-be-converted substrate is achieved using metal-loaded zeolite powders, as is the case in selective catalytic reduction of NOx using Cu-based zeolites. Moreover, with the emerging shift towards a sustainable and renewable refining and petrochemical industry, the use of tailored-metal based containing catalysts is likely to intensify. Zeopore has achieved to combine high-quality mesopore formation with a controlled and highly tunable metal deposition. The method can be applied to any zeolite and most non-noble metals. Resulting metal-containing zeolites can then be shaped into catalysts, such as extrudates afterwards. Hence, the method of metal deposition is fundamentally different compared to standard metal-containing catalysts [1], in which first an extrudate is made, to be subsequently complemented with a metal using in an impregnation step.

The unique properties of Zeopore's metal-containing zeolites become obvious from almost any method of characterization. In the contribution, we will use various case studies, on for example Mg-ZSM-5, Mg-ZSM-23, and Ni-USY on both the powder and the extrudate level, to demonstrate how this class of materials contains superior porous properties, improved metal dispersions (near 100% dispersion), unique acidity profiles, and increased (hydro)thermal stability, using a variety of analytical techniques, such as N2 sorption, FTIR spectroscopy with adsorbed pyridine, elemental analysis, chemisorption, and electron microscopy. Obviously, the proof of the pudding is in the catalytic performance. Zeopore is currently actively exploring the potential of this type of metal-containing zeolites in a number of applications, such as hydrocracking, dewaxing, methanol conversions, and aromatics conversion. We will demonstrate outstanding results in diesel dewaxing by hydro-isomerization using unidirectional zeolites, attaining -over standard mesoporous zeolites [2]- an order-of-magnitude lower diesel losses as a function of cloud point improvement and a simultaneous unique hydrogenation performance of aromatics present in the diesel feed. Also, a case on Mg-containing ZSM-5 in methanol to propylene will be demonstrated, evidencing, besides the expected 3-to-5-fold lifetime enhancement, an over 20% increased selectivity to propylene. The latter being not obvious after post-synthetic mesoporization [3]. Based on the convincing materials and catalytic results, Zeopore is currently exploring the potential, in particular with potential users, such as refiners, zeolite and catalyst manufacturers as well as petrochemical companies. Moreover, especially in the emerging -yet demanding- sustainability-based applications, this technology fits like a glove.

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1113 - PROBING THE ACTIVE SITES OF DEFECT ENGINEERED UIO 66 BY FTIR SPECTROSCOPY

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UiO-66 is a metal-organic framework applied in catalysis, gas storage, drug delivery, etc. [1]. Zirconium ions in this MOF are bonded via bridge µ3-O and µ3-OH groups, forming Zr6O4(OH)4 clusters. During thermovacuum treatment, zirconium clusters lose 2H2O molecules and transform to Zr6O6 with six µ3-O groups. Strong Zr-O covalent bonds and high coordination numbers make UiO-66 extremely tolerant to the high concentration of defects in the structure. The coordination modulator approach is one of the ways to introduce defects. According to this technique, monocarboxylic acid (modulator) competes with terephthalic acid for Zr coordination [2]. Because the modulator has only one carboxylic group, it is not able to connect two Zr clusters. Coordination of the Zr-site with monocarboxylic acid creates defect sites in two opposite Zr-clusters forming a missing-linker defect. Consolidation of missing-linker defects (high modulator concentration) results in the generation of missing-cluster defects. Defects modify UiO-66 properties in different ways [3]. However, direct observation of defect sites is still a challenging task.

Here we present a comparative IR spectroscopic study of UiO-66 with and without defects. Three samples were obtained using solvothermal synthesis. UiO-66-0BA sample was produced without a modulator and resulted in aggregated nanoparticles. UiO-66-10BA was synthesized with 10 eq of benzoic acid resulting in highly porous nanoparticles with missing-linker defects. UiO-66-60BA was obtained with 60 eq of benzoic acid and contained highly porous micron crystals with missing-cluster defects. For the IR studies, the sample pellets were activated at 275 oC in order to remove DMF residues, then hydroxylated and evacuated at r.t. With all samples, we detected µ3-OH groups (3677 cm-1). Low-temperature CO adsorption showed these OH groups are of weak acidity (ΔνOH = 74-79 cm-1) and are the only CO adsorption sites. However, the use of CD3CN as a probe (able to replace water) revealed some Zr4+ sites, but only with the UiO-66-0BA sample. This was associated with the imperfection in the UiO-66 framework due to the fast nucleation. The dehydration process of the Zr-clusters was followed as a function of the evacuation temperature. CO as a probe indicates a slight increase in OH's acidity with dehydroxylation. No Zr4+ sites were detected on UiO-66-10BA and UiO-66-60BA samples even after 275 oC evacuation. This shows that Zr4+ sites remain linked to benzoate groups and are thus coordinatively saturated. A small amount of Zr4+ sites were detected with the UiO-66-0BA sample; the same was observed at r.t. by CD3CN.

Interestingly, Zr4+ sites were detected by CD3CN with all samples evacuated above 150 oC, and the amount of these sites increased with the dehydroxylation degree. Because these sites were invisible by CO, we stress that CD3CN, being a stronger base than CO, causes some structural changes in the zirconium clusters. Thus Zr4+ ions originally holding OH groups can be tested.

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CATEGORY: AIR AND WATER CLEANING

1074 - REMOVAL OF LOW TRACE PPB LEVEL PERFLUOROOCTANESULFONIC ACID (PFOS) WITH ZIF 8 COATINGS INVOLVING ADSORBENT DEGRADATION

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Per- and poly-fluoroalkyl compounds (PFAS) are group of anthropogenic and environmentally persistent organic chemicals, composed of hydrophobic-oleophobic aliphatic alkyl chain with the hydrogen atom either totally (per-) or partly (poly-fluoroalkyl) replaced by fluorine atoms [1]. These compounds though widely used in industrial and commercial applications as surfactant, are considered top priority pollutants [2]. Recently, ZIF-8 has also been suggested as promising candidate for removal of per- and poly-fluoroalkyl compounds (PFAS)[3,4]. However, besides the limited literature two major gaps are identified. First, the PFOA/PFOS removal adsorption experiments on ZIFs were performed at higher initial concentration (100 – 500 mg/L)][3,4] than those environmentally relevant (µg/L level)[2]. So, even though high sorption capacities have been reported, the equilibrium PFAS concentration of the aqueous solution remains significantly (> 100 times) above the limit imposed by the EU directive 2020/2184 (0.5 µg/L)[1]. Secondly, no clear understanding of the adsorption mechanism has been proposed. While Chen et.al. concluded that crystal structure and surface functionality are important parameters affecting PFOA adsorption on ZIFs [3], no major insight in the PFOS adsorption mechanism on ZIF-8 and ZIF-67 were provided in the study by Konno et.al.[4].

In this work, we report low trace level removal of PFOS i.e., 20 – 500 µg/L (ppb), from aqueous media by using a ZIF-8-based structured adsorbent. A ZIF-8 coated copper sheet (ZIF-8@Cu) composite was synthesized following a direct in-situ synthesis route at room temperature and was employed for PFOS removal when present in low trace ppb level concentration. The ZIF-8 coated copper sheet showed the highest removal rate (98 %) in comparison to different commercial AC and all-silica zeolites. The removal rate remained consistent over a wide range of concentration and additionally, no adsorbent leaching from the composite was noticed, which eradicated the need of additional steps such as filtration, centrifugation, unless needed for other adsorbents studied here. The composite displayed fast uptake with saturation reaching within 4h, irrespective of the initial concentration. However, the morphological and structural characterization revealed surface degradation of ZIF-8 crystals, along with a decline in the crystal size. The adsorption of PFOS on the ZIF-8 crystals was attributed to chemisorption, as the surface degradation surges with increase in PFOS concentration or with cyclic exposure at low concentrations. Methanol seemingly removed surface debris (partially), thus providing access to ZIF-8 beneath surface debris. Overall, the findings demonstrate that at low trace level PFOS concentrations ZIF-8 can be considered a possible candidate for PFOS removal, as though it suffers slow surface degradation, it also removes efficiently PFOS molecules from aqueous solutions.

1079 - CAPTURE OF VOCS FROM FOREST FIRES BY ZEOLITIC ADSORBENTS

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Every year, over 5000 forest fires are recorded in France [1], mainly in the Mediterranean South because of the hot and dry climate. The smoke emitted during these fires is composed of numerous substances, including volatiles organics compounds (VOCs) [2]. Depending on their nature, their concentration and the duration of exposition, these VOCs can cause hazardous effects on the environment and on the health of firefighters who are exposed to the smoke during wildfires [3]. In addition, the inhalation of fumes can result in a broad spectrum of pulmonary diseases.

The main objective of this work is to evaluate the performance of hydrophobic zeolite materials to capture VOCs emissions from forest fires.

The VOCs formed during the wood thermal oxidation were analysed using a thermodesorber coupled to a gas chromatograph equipped with a mass spectrometer detector (TD-GC-MS). The chromatograms show that many volatile organic compounds such as, aromatics, aldehydes, alkanes, ketones, were emitted during wood thermal oxidation. A selection of seven molecules representative of each class of organic compounds was considered in this study: cyclohexane, methyl ethyl ketone, toluene, octane, methyl acetate, propanal, 2-methyltetrahydrofuran. Considering the size of the selected molecules, three types of hydrophobic zeolite with different pore sizes were chosen: MFI, FAU and *BEA. The adsorption properties of these solids were studied at equilibrium by McBain thermogravimetry and under dynamic condition using the breakthrough curves measurements.

The adsorption isotherms of low polar VOCs (cyclohexane, toluene, octane) and polar VOCs (butanone, methyl acetate) on zeolites will be presented and compared to those obtained on a reference activated carbon. The hydrophobic nature of these materials was evaluated by water vapor adsorption. The data analysis shows that at a VOC concentration of 1000 ppm, the quantities adsorbed by zeolites increase according to the following sequence: FAU > *BEA > MFI. The capacities of these materials will be related to their physicochemical properties (pore size, specific surface, micropore volume, hydrophobicity, ...), in order to define the most efficient material. The performances of the used zeolite adsorbents for capture of VOCs in dry or humid air under dynamic conditions will also be presented.

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1213 - A COMBINED COMPUTATIONAL AND EXPERIMENTAL APPROACH TO PREDICT NOX AND CO ADSORPTION TO AGX APPLICATION TO THE DIESEL ENGINES

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The aim is to reduce the emission of gaseous compounds from exhaust gases. Catalytic solutions exist to reduce toxic species. These solutions are not well functional during the cold start cycle. Therefore, it is necessary to develop a process to capture toxic gas at low temperature. However, water, which is into the exhaust gas, inhibits sometimes the adsorption of pollutants. Nowadays, the accuracy of DFT (Density Functional Theory) calculation is high enough to predict adsorption enthalpies of various molecules in zeolites. They have been performed for a systematic screening through a series of monovalent cation-exchanged X faujasite zeolites and subsequently evaluated for their ability to capture CO, NO and NO2. In the present work, the computational cell containing 144 atoms has been adopted to reduce the computational effort. However, this numerical tool requires an experiment validation therefore isotherm measurements were carried out to reach enthalpy adsorption at “zero loading”. To investigate the adsorption selectivity, the single-component adsorption isotherms were measured experimentally by manometry at three temperatures with pressure which varied from 0 to atmospheric pressure, P0. To determine the adsorption enthalpy according the loading, the isosteric method is used. Moreover, dynamic experiments have been carried out to study the co-adsorption. The adsorption of pure NO, NO2 and CO and their mixtures with and without water and oxygen gas is studied at 101.3kPa and 303K. Otherwise, experiments was carried out with NaX to propose a comparison between Ag+ and the common sodium compensation cation. The aims were to evaluate (i) the breakthrough times, (ii) the amount of species adsorbed and (iii) the reasons that lead to surface chemical reactions.

Equilibruium experiments showed that AgX zeolite can be used to trap CO, NO and NO2.The adsorption capacities increased in the following order: NO < CO < NO2. DFT calculations are in agreement with equilibrium experimental results. The adsorption energy of these three pure species at zero coverage has the same behavior. We can observe that NO2 is more adsorbed than water with an enthalpy difference around -30 kJ/mol. Otherwise, calculations performed on Ag+ demonstrate a high affinity for NO and CO gas molecules exceeding -70 kJ/mol. However, the adsorption energy of water on AgX is respectively higher than, and equivalent to that of NO and CO molecules. Dynamic experiments carried out allowed showing that AgX is (i) easily regenerable for further reuse, (ii) offering long-term stability and (iii) allows to trapping CO, NO and NO2. However, chemical reaction occurs between NO2 and water to generate NO; but NO is adsorbed thanks to zeolite AgX. To conclude, the breakthrough model and experiments supported by DFT results, indicated that this approach can be applied for improving the design, scaling up and optimizing the continuous fixed-bed adsorption systems to treat exhaust gases.

1238 - PT ZEOLITES AS ACTIVE CATALYSTS FOR THE HYDROGENATION OF CHLORATES IN WATER PHASE

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Water is essential for life and it is necessary to guarantee their quality, mainly when is used for human drinking. Nowadays, this is achieved by different disinfection treatments, most of them based in the use of chlorine compounds. However, this process can produce by-products such as chlorite and chlorate that have negative effects on health. For these reasons, the World Health Organization set a provisional limit of 0.7 mg L-1 for both pollutants in drinking water. Different techniques can be used for the control of these pollutants as adsorption, ion exchange, membranes but they generate wastes that must be treated. An alternative to these separation processes is the catalytic reduction of oxy-chlorine anions with hydrogen forming innocuous Cl-, according to [1, 2]:

$$ClOx- + xH2 \rightarrow Cl- + xH2O$$

Catalysts were prepared by incorporating platinum to different zeolites (FAU, BEA, MWW and MOR) by different processes as coprecipitation, ion exchange and wetness impregnation. Catalysts were activated with hydrogen at 200ºC before reaction and the experiments were performed in a batch stirred tank reactor at room temperature and atmospheric pressure, using hydrogen as a reducing agent. The typical experiments were made with 1 g of catalyst and 0,6 L of polluted water with 50 ppm of chlorate. The catalytic activities of the Pt-zeolites were compared with a reference catalyst based on Pt-Al_2O_3. The analysis of the reactants and products was made by ionic chromatography. The catalysts were characterized with different techniques such as inductively coupled plasma (ICP), X-ray diffraction (XRD), temperature programmed reduction (TPR) and N2 adsorption.

The catalytic experiments have shown that zeolite topology, zeolite Si/Al ratio and presence of sodium in the zeolite are the main factor influencing the catalyst activity. It was observed that better results were obtained with faujasite due to its improved accessibility, consequence of the presence of big cavities and to the 3D structure that favour the diffusion of reactants and/or products. Other important characteristic to be considered is the Si/Al ratio of the zeolite, observing that zeolites with lower Si/Al ratio results in more active catalysts. These results are related with a better dispersion of the metal on the zeolite surface in zeolites with a higher number of Lewis acid sites. Finally the presence of sodium in the zeolite was also investigated observing that when the sodium content was increasing then the activity of the zeolite was decreasing. This was related with an enhanced facility for platinum agglomeration in presence of Na+.

The influence of the platinum content and the influence of the procedure used for Pt incorporation have also studied. It was observed that although the reaction rate increases with the increase of the metal content, the TOF decreases due to a lower dispersion of the metal active sites. Similarly better results have been obtained when the Pt has been incorporated by ion exchange as in this way a better dispersion of the active sites is achieved.

Then, from the results obtained it may be concluded that there is strong influence of the type of zeolite, of its Si/Al ratio and of the sodium content on the catalyst activity as these parameters influence on the metal dispersion and consequently on the catalyst activity. The best results have been obtained with the catalyst supported on zeolites with a high number of acid sites and with accessible structures. These characteristics improve the dispersion of platinum and favour the interaction of the reactants with the active centres. In this way, the best results have been obtained with the catalyst supported on FAU with a Si/Al ratio of 6 that is an active and stable material able to reduce the chlorates in successive reaction cycles without important deactivation.

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1242 - EFFICIENT TOP DOWN STRATEGY FOR SYNTHESIS OF CATALYTICALLY ACTIVE CO3O4 NANOPARTICLES TRAPPED IN WELL COMMUNICATED MESOPOROUS SILICA SHELLS

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Various types of core-shell materials, including multicore@shell or core@multishell structures, have recently gained a lot of interest due to their unique properties used e.g. in the catalytic removal of volatile organic compounds (VOCs) [1]. Among them, yolk shell structures appear to have many advantages, such as providing high dispersion of active phase nanoparticles inside hollow, porous spheres and protecting them against aggregation at elevated temperatures [2,3]. The space available inside the shells facilitates free contact of components of reaction mixture with the active sites. Furthermore, the described arrangement guarantees rational transport of heat (including heat released during exothermic combustion reactions) in a catalytic bed, resulting in reduction of local overheating effects and protection against the formation of hot spots during the catalytic process. In the presented work, nanostructures containing catalytically active Co3O4 spinel nanoparticles surrounded by SiO2 shells are examined. In comparison to conventional catalysts that contain the Co3O4 active phase deposited on a SiO2 support, the proposed yolk-shell structure provides a better access to the surface of active phase nanoparticles, which results in higher activity and selectivity in the VOCs combustion.

Spherical particles of diethyltriamine-functionalized poly(maleic anhydride) (MA-DETA) and polystyrene (PS) with uniform diameters within the range of 200-240 nm were synthesized. Subsequently, the polymer template was surrounded by a SiO2 precursor using the modified Stöber strategy. An influence of type of solvent, amount of SiO2 precursor, TEOS/NH3 ratio and addition of surfactant on quality of the formed coatings was tested using scanning electron microscopy (SEM). As the result of SiO2 deposition optimization, the spherical silica materials with high specific surface area (SBET value above 1100 m2/g) were obtained, containing mesopores enabling access to their interior. In the next step of the synthesis, a transition metal oxide (Co3O4) precursor was incorporated into the polymer@SiO2 materials using various approaches, including wet impregnation and adsorption process. The kind of modification method and the amount of the introduced Co3O4 precursor determined properties of the active phase created within the yolk-shell structures. The structure, composition and reducibility of the Co3O4-containing materials were studied by XRD, XRF, UV-Vis-DR, XPS and H2-TPR. In addition, the synthesized catalysts were tested in the total oxidation of toluene, which was selected as a model aromatic hydrocarbon. It was shown that the yolk-shell materials containing the Co3O4 phase exhibited very high catalytic activity in the tested reaction. The selection of the polymer template used for the synthesis of SiO2 spheres had a significant impact on the catalytic activity. The catalysts prepared on the basis of the MA-DETA template were characterized by significantly better catalytic activity compared to those constructed on the PS grains. Differences in the catalytic activity were related to the dispersion of Co3O4 nanoparticles inside the silica spheres. The high dispersion obtained in the case of using the MA-DETA matrix resulted from the presence of amino groups, which ensured the appropriate adsorption capacity of Co3+ ions introduced during the modification. As a result, extremely active systems were achieved, far exceeding those described in the scientific literature.

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1260 - USE OF ZEOLITES FOR FUTURE AUTOMOTIVE EMISSIONS CONTROL

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Nowadays, modern vehicles have much cleaner and more efficient combustion processes with improved fuel injection system design and sophisticated engine management systems. However, the impact of air quality on human health, particularly in urban environments, is of great importance for the development of these technologies. The demand for cleaner urban air and massive reductions in CO2 and other GHG emissions is increasing both from the public and from regulators and governments in many countries and regions. Net zero GHG targets have been set and legislated in several geographies, and more are clearly going to follow in the coming months and years. Transportation is currently a major emitter of criteria pollutants (including CO2, CO, hydrocarbons, NOx, and PM) and this sector still requires more research and development for lean-burn gasoline, diesel engines, and engines burning a range of alternative fuels. [1,2] Euro 6 passenger car legislation, which came into effect in September 2014, more than halved the permitted NOx emissions and thus led to the introduction of specific NOx control technologies on almost all new European passenger vehicles. However, recently proposed regulations from Euro 7 are a new step for cleaner transport and a zero-emission world and will require about a 20% decrease in NOx emissions. [3] Therefore, the development of new catalysts with good tolerances to the above emissions and process parameters is of great significance for further reducing NOx from diesel engines. In this context, zeolite catalysts exhibit high catalytic performance and hydrothermal stability due to their unique pore size structure and large specific surface area, especially microporous zeolite catalysts. Zeolite-based technologies include NH3 SCR for NOx reduction over a wide temperature window, hydrocarbon traps for low-temperature emissions control, and ammonia slip catalysts (ASCs) to help with the release of excess ammonia into the atmosphere. However, zeolite catalysts are still facing many challenges because of the increasingly strict emission standards, as well as to extend practical applications, such as improving the catalytic performance, increasing hydrothermal stability, and reducing cost. [4] The presented work will aim to elaborate on current zeolite-based technologies and provide an overview of future legislation demands.

1348 - METHODS FOR IMPROVING THE GASEOUS IODINE UPTAKE AND STABILIZATION IN MOF MATERIALS

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Titanium-based Metal-Organic Frameworks (MOFs) are a well stablished family of MOFs that are particularly interesting due to their redox activity, photocatalytic properties, and low toxicity. MIL-125 is an example of a highly porous Ti-MOF constituted by a quasi-cubic tetragonal structure formed by TiO5(OH) octahedra and 1,4-benzenedicarboxylate BDC linkers [1]. Its parent, MIL-125(NH2), can be obtained by functionalizing the BDC linker with amino groups. Both MIL-125 and MIL-125(NH2) can be employed, among other possible applications, for the adsorption of gaseous pollutants. To the authors' knowledge, there is to date no mention in the literature of the use of a MIL-125 compound for the adsorption of I2 gas. Therefore, the adsorption of I2 by MIL-125 and MIL-125(NH2) was studied after synthesis of the materials. Furthermore, to assess the titanium influence on the I2 capture, an aluminium-based MOF, CAU-1, which is isoreticular to the MIL-125 compounds was also synthesized. The prepared compounds were characterized using powder XRD, vibrational spectroscopies (FTIR and Raman), diffuse reflectance UV-Vis spectroscopy, N2 sorption measurements, and EPR spectroscopy. A colour change was first observed after contact between the MOFs and the gaseous iodine: from white to orange in MIL-125, and from yellow to orange-brown in MIL-125(NH2) and CAU-1. This feature was studied in depth by using UV-visible absorption and Raman scattering which allowed to highlight the presence of I2 and I3- species. In particular, a kinetic investigation was conducted by Raman spectroscopy to evaluate the transformation of I2 into I3- after contact between MOFs and I2 by assessing their respective contributions within the structure of the materials. Using EPR experiments, it was also shown that a linker-to-metal charge transfer (LMTC) related to the reduction of the Ti4+ sites to Ti3+is photoinduced in the Ti-based compounds upon irradiation of the MOF in the absence of I2 (Figure 1). However, it is interesting to note that the photo-irradiation of the MIL-125 adsorbed with iodine lead to a significant decrease of the spectral signature of Ti3+, demonstrating that I2 interferes with the electron transfer inside MIL-125 compounds. Finally, the stability of the different species was verified by in-situ Raman desorption experiments at different temperatures (40, 60, 80, and 100 ºC). Here, the rate constants corresponding to the desorption of I2 and I3- were calculated and used to assess the desorption energies for these two species by means of the Arrhenius equation. In this way, the influence of amino and titanium over the stability of the iodines species was evaluated.

1176 - MITOXANTRONE DERIVATIVES AS DRUG STRUCTURE DIRECTING AGENTS FOR THE SYNTHESIS OF MSNS FOR BREAST CANCER TREATMENT

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Cancer causes hundreds of thousands of deaths worldwide each year. Chemotherapy appears as the most chosen treatment for invasive cancers, but severe side effects related to off-target exposure limit its dosage and thus its efficacy. Mitoxantrone (MTO) has largely proven its effectiveness in the treatment of metastatic breast cancer (MBC) , but its usage is limited by the related toxicities [1]. Nanomedicine has emerged as a potential tool to overcome these problems: the encapsulation of the chemotherapeutic drugs in nanocarriers that may be targeted to the tumour appears as a promising tool to avoid unwanted effects and to increase its efficacy. Among the nanocarriers, mesoporous silica nanoparticles (MSNs) have attracted much attention due to its high surface area (up to 1000 m2 g-1), the versatility in size and pore diameter, and its ease of functionalization. However, premature drug leaking from the MSNs usually occurs, so the drug is released before the nanocarrier achieved its target, decreasing its effectiveness and appearing adverse effects. Different strategies have been developed to prevent premature drug release, such as the introduction of different moieties in the MSNs to increase the cargo-vehicle interaction.

Our group has developed a new method to increase drug loading capacity while preventing premature drug release. This novel strategy consists of the use of a drug structure-directing agent (DSDA) which plays a double role, acting as pharmacological prodrug and as a template for the synthesis of MSNs [2]. For this purpose, the drug must be modified to bear a non-polar chain to create an amphiphilic molecule where the drug is the polar head. Drug loading capacity of DSDA-MSNs was maximized since all the mesopores were totally fulfilled by the DSDA. Besides, the synthesis of this novel DSDA-MSNs does not require either the surfactant removal step or the posterior drug loading one.

In this work, we synthesized and fully characterized two MSNs using two different MTO-derivatized molecules to be used as DSDA. For this purpose, a C12 hydrocarbon chain and a C18 oleyl chain were covalently bounded to MTO. Spherical and nanometre sized MSNs were obtained by using both MTO-DSDA as a surfactant, named MTO-C12@MSNs and MTO-C18@MSNs. The amount of drug loaded was as high as 630 mg of drug per gram of MTO-C12@MSNs and 250 mg in the case of MTO-C18 @MSNs. The drug-release profile of both materials was studied in vitro showing pH-responsiveness: the MTO-DSDA release did not occur at physiological pH, but an acidic medium remarkably enhanced the deliverance. Besides, the efficacy of the MTO-DSDA@MSNs on reducing cancerous cells viability was assayed on 2-D cell cultures, proving that MTO-DSDA@MSNs produced a decrease in cellular viability. Therefore, these results make MTO-DSDA@MSN a promising material to increase MTO efficacy, while reducing drug premature release and thus side effects.

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1148 - L ARGININE CONTAINING MSN (ARG@MSN) EMBEDDED IN DENTAL ADHESIVE FOR TARGETING CARIOGENIC BACTERIA

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Nowadays, the development of Mesoporous Silica Nanoparticles (MSNs) results very attractive due to their numerous applications in several fields, such as catalysis or biomedicine. In this last field, these MSNs have become an essential tool in drug delivery for their ability to allow a controlled and selective release of different drugs incorporated into their structure. MSNs present outstanding properties, such as their high surface area, ease functionalization and a specific pore volume that permits the easy loading of a vast array of pharmacological compounds showing, besides, good in vivo biocompatibility. Recently, our group has reported a novel concept termed Drug Structure-Directing-Agents (DSDA), based on the use of molecules with biological activity as surfactants addressing the MSN synthesis [1].

In this work, we have synthesized a DSDA derived from the aminoacid L-arginine, which is then used to developed MSNs (Arg@MSN) as a drug delivery system incorporated into a dental adhesive (Arg@MSN@DAdh), with the aim of the long-term L-arginine delivering in a controlled way and thus neutralizing the proliferation of cariogenic bacteria caused by the decomposition of the classical adhesive resin composites used in the treatment of caries [2]. Arg@MSN@DAdh can neutralize the harmful acidic conditions that produce the apparition of dental secondary caries when the decomposition of the dental adhesive takes place [3]. The obtained in vitro results have shown the reduction of the population of the bacterial strains Streptococcus mutants and Lactobacillus casei, preventing the biofilm formation over the adhesive surface, and demonstrating the efficient growth inhibition caused by the slow and sustained release of the L-arginine from MSN and its diffusion out the dental adhesive. Moreover, the mechanical and bonding properties of the dental adhesive did not suffer significant changes after the incorporation of Arg@MSNs. These good results make these MSN-dental adhesive hybrid systems (Arg@MSN@DAdh) as potential cost-effective candidates for dental caries restoration.

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1025 - DEVELOPMENT OF MACHINE LEARNT POTENTIALS FOR MOLECULAR DYNAMICS SIMULATIONS OF AMORPHOUS METAL–ORGANIC FRAMEWORKS

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There is an increasing interest in the amorphous states of metal-organic frameworks (MOFs) and porous coordination polymers, which can be produced by various routes (under the application of pressure, temperature, etc). Amorphous MOFs can exhibit useful physical and chemical properties, distinct from those achievable in the crystalline states, along with greater ease of processing, and intrinsic advantages over crystals and powders, such as high transparency and mechanical robustness. However, these amorphous states are particularly challenging to characterise, and the determination of their framework structure at the microscopic scale is difficult, with only indirect structural information available from diffraction experiments. As of today, an array of methods coexists to model these disordered materials, with a lack of direct and in-depth comparison in the existing literature. [1]

One strategy consists in simulating the phase transition from a crystalline MOF to the amorphous state using molecular dynamics (MD). While ab initio MD has successfully been used to model the melting of MOFs and their liquid phases, its significant computational cost has limited its use to small systems on rather short time scales (tens to hundreds of ps), calling for the development of more computationally tractable approaches. Classical MD simulations, routinely used for crystalline MOFs, are not a straightforward option as they are unable to simulate bond breaking or reformation, two processes inherent to the formation of most amorphous MOFs. ReaxFF reactive force fields have been proposed in several studies to generate models of MOF glasses but feature an unphysical description of the local coordination environment. [2]

In our work we have developed Machine Learnt (ML) Potentials for amorphous MOFs using NequIP [3] that we propose as a new generation of specific and accurate reactive potentials. Built from ab initio data, these potentials enable bond breaking and reformation by design and lead to an excellent reconstruction of the structural properties. We have demonstrated how they can be used to generate models of MOF glasses by melt-quenching, and extensively compared the resulting structures to glasses obtained in previous studies. In addition, by generating a sizeable training set made of ab initio MD trajectories of several phases of multiple MOFs, at various temperatures and volumes, we investigated the transferability of the ML potentials and evaluated the impact of diversity in the explored phase space. Finally, we studied the incorporation of stresses in the learning procedure and computed several mechanical properties of interest that were contrasted with values calculated with previously available MD schemes.

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1028 - INTERNAL HYDROGEN BONDS OF H–MFI

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Knowledge about type and position of active sites in zeolites is a prerequisite for the rational design of catalysts and catalytical processes. We provide evidence for the presence of H–bonded bridging hydroxyl (b–OH) groups in the zeolite H–MFI. Nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy indicate multiple structurally different proton sites.[1,2] The 1H–NMR signal at 4.2 ppm and IR signal at 3614 cm–1 are commonly attributed to free b–OH groups.[1] The assignment of 1H–NMR and IR signals at 7.0 ppm and 3250 cm–1, respectively, is debated with previous reports assigning them either to H–bonded b–OH groups [2] or to defect sites or residual water.[3] Using our chemically accurate QM:QM embedding methodology (QM = quantum mechanics) which goes beyond standard calculations based on density functional theory (DFT), we show that these signals can originate from H–bonded framework b–OH groups.

The MFI framework features 12 crystallographically unique sites for aluminium substitution. A proton can be located at each of the four oxygen atoms surrounding the aluminium atom, resulting in a total of 48 b–OH isomers in the ideal H–MFI structure. Further, we find that multiple conformers exist for b–OH isomers due to H–bonding to different Si–O–Si acceptor sites. Since the aluminium distribution is most likely not thermodynamically controlled, calculating relative stabilities of all b–OH isomers and their conformers does not suffice to identify which active sites are present in real H–MFI samples.

We overcome this hurdle in two steps. First, we calculate chemically accurate relative stabilities and the corresponding structures for all b–OH isomers. Choosing the most stable b–OH isomers at each aluminium substitution site yields a set of probable b–OH groups of which some are free and other H–bonded. Second, we calculate accurate 1H–NMR and IR spectroscopic features for this selection. The predicted 1H–NMR and IR signals for the free b–OH groups range from 3.9 to 4.5 ppm and from 3614 to 3628 cm–1, respectively. This is in good agreement with the experimental signals at 4.2 ppm and 3614 cm–1, respectively, validating the accuracy of our predictions. The predicted 1H–NMR and IR signals for the H–bonded b–OH groups range from 4.7 to 10.3 ppm and from 3016 to 3585 cm–1, respectively, agreeing well with the broad experimental peaks centred at 7.0 ppm and 3250 cm–1, respectively. The length of internal H–bonds varies substantially with their framework position which reflects in a wide spread of predicted 1H–NMR and IR signals.

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1039 - REACTIVE NEURAL NETWORK POTENTIALS FOR VARIOUS CLASSES OF ZEOLITES

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Neural network potentials (NNPs) are becoming increasingly popular in multiple areas of material science and chemistry thanks to their ability to keep ab initio accuracy at the cost of the standard reactive force fields such as ReaxFF [1]. However, the vast majority of the studies focused on systems with rather low-dimensional configurational space such as elemental systems, a specific chemical reaction or a more complex system but close to a particular thermodynamic state point. This apparent curse of dimensionality could be behind the fact that NNPs for microporous solids such as zeolites are, to the best of our knowledge, practically non-existent [1].

In this work, we present the development of a more general (global) reactive NNPs using the SchNet architecture [2] for various zeolite classes using robust training and data curation procedures. The resulting NNPs retain density functional theory (DFT) accuracy across the complex zeolitic classes considered, outperforming specialized ReaxFF by order(s) of magnitude in accuracy, while speeding-up calculations by at least three orders of magnitude compared to DFT.

Up to now we have managed to generate NNPs for multiple systems including: i) siliceous zeolites (including silica glass), for which we carried out large-scale screening of zeolite databases (>330k hypothetical zeolites) revealing more than 20k additional hypothetical frameworks in the thermodynamically accessible range for zeolite synthesis [3], ii) germanosilicate zeolites, for which we studied effect of zeolite topology on germanium clustering propensity with profound effects on their delamination propensity [4], iii) platinum clusters embedded in (defective) siliceous zeolites, for which we studied the role of zeolite topology on stability and migration pathways of these metal clusters [5], iv) aluminosilicate zeolites in acidic form interacting with neutral/acidic/basic aqueous solution, for which we looked at the effect of aluminium content, water loading and temperature on water diffusion and proton solvation in H-FAU zeolite [6], and v) aluminosilicate zeolite in sodium form interacting with neutral/acidic/basic aqueous solution, which enables us tackle the process of zeolite synthesis itself. Importantly, the NNPs for more complex systems (e.g., for the aluminosilicate zeolites) are applicable for the simpler constituent systems (e.g., for the defective siliceous zeolites), i.e., our NNPs truly tend towards global NNP potentials.

Lastly, our recent work [7] suggests that the learned NNP representations of atomic environments, a by-product of our NNP generation, can be reused to construct robust collective variables (CVs) that are "aware" of the underlying potential energy surfaces - such CVs used in conjunction with the herein developed NNPs may not only accelerate but also largely automatize generation of realistic free energy surfaces of reactive processes in zeolitic systems. Therefore, the herein developed, reactive zeolite NNPs enable calculations of complex zeolitic frameworks under experimentally relevant conditions and may enable not only high throughput calculations for the targeted zeolite design but also provide atomic-level insights into zeolite synthesis and stability.

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1042 - ATOMISTIC MODELLING APPROACHES TO STUDY THE ADSORPTION OF EMERGING ORGANIC CONTAMINANTS IN HYDROPHOBIC ZEOLITES

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Pharmaceuticals and personal care products (PPCPs) are currently receiving considerable attention as environmental pollutants. Although environmental concentrations are typically very low, negative effects on the environment and, indirectly, on human health (e.g., through development of microbial resistances) cannot be ruled out. The adsorption-based removal of PPCPs during wastewater treatment appears as a highly promising option to prevent their release into the environment. Among potential adsorbents, carbon-based materials are most widely studied, which are attractive due to their low cost and the ability to adsorb a broad range of contaminants in the micro- and mesopores. They do, however, possess some disadvantages, such as limited regenerability and the risk of pore blocking by natural organic matter. Hydrophobic high-silica zeolites have hence been proposed as a potential alternative for PPCP removal [1]. Although it appears rather unlikely that zeolites will be used in bulk applications aimed at the removal of organic contaminants from wastewaters due to their high cost, their well-defined pore sizes and shapes could render them very attractive for applications targeting a highly selective removal of individual species or groups of species.

Given the vast number of possible combinations of zeolites and PPCPs, experimental liquid phase adsorption studies are possible only for a limited subset of such combinations. Computational modelling techniques can help to identify combinations of interest prior to a targeted experimental characterisation. In addition, the calculations can also provide insights into the dominant interactions governing the adsorption behaviour, improving the molecular-level understanding. This contribution will present results from recent computational studies of PPCP adsorption at different levels of theory. On the one hand, a large number of zeolite-PPCP combinations were screened using molecular dynamics simulations, employing force field parameters that were validated against dispersion-corrected density functional theory (DFT) calculations. Building on a previous, less comprehensive study [2], this investigation combined a wide range of relevant PPCP contaminants with various zeolite frameworks that are available in highly siliceous form. On the other hand, dispersion-corrected DFT calculations were used to study the adsorption of two contaminants of particular interest, carbamazepine and triclosan, in different zeolites. The first of these studies, which exclusively considered all-silica zeolites, looked at the impact of pore topology on the affinity towards carbamazepine. Moreover, the respective contributions of host-guest and guest-guest interactions were analysed [3]. A subsequent DFT investigation addressed the adsorption of triclosan in all-silica zeolites and protonated zeolites with high Si/Al ratios. Although the presence of framework protons resulted in an enhanced affinity towards triclosan, the affinity towards water increased even more markedly, indicating that competitive water adsorption is likely to block the framework protons as adsorption sites.

On the basis of these results, it will be discussed how atomistic simulations can contribute to the development of zeolite adsorbents for PPCP removal, and which aspects deserve particular attention in future computational chemistry studies dealing with the adsorption of functional organic molecules in zeolites.

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1050 - METHANOL DYNAMICS IN METHANOL TO HYDROCARBON ZEOLITE CATALYSTS – A MOLECULAR DYNAMICS AND QUASIELASTIC NEUTRON SCATTERING STUDY

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Establishing sustainable catalysts and processes to achieve renewable energy sources and reduce environmental impact is a pressing matter for the development of our society. CHA-type zeolites, specifically SAPO-34, are established as leading catalysts in the methanol-to-olefins (MTO) reaction and are thus of great interest to both academia and industry as the demand for light olefins is ever increasing, and the scarcity of petroleum reserves renders the conventional cracking of crude oil fractions unlikely to satisfy such demands. The CHA framework is a 3-dimensional microporous system with an accessible 3.8 × 3.8 Å window of eight-membered ring cavities making them excellent catalysts to produce C2-C4 light olefins due to shape selectivity. The initial step in catalysis involves the diffusion of methanol through the zeolite framework to the active site, followed by interactions with Brønsted acidic sites through hydrogen bonding. An understanding of the molecular mobility of methanol within the zeolite framework is of great importance in understanding the catalytic process, and the effect that catalyst structure and composition has on such behaviour is therefore of significant interest.

Methanol diffusion in ZSM-5 was studied using classical molecular dynamics (MD) at 373-423 K, using loadings of 3 and 5 molecules per unit cell, in frameworks with Si/Al = 15, 47, 95, 191 and a siliceous system. While the lower loading exhibits higher diffusivity, self-diffusivities increase at both loadings between Si/Al = 15 and 95, after which they are independent of composition. The trend in diffusivity with Si/Al ratio is explained in terms of methanol-acid site interactions, while the trend with loading is explained in terms of methanol-methanol interactions and the resulting methanol structure in the catalyst pores. Our previous work probing the effect of Si/Al ratio on methanol mobility in zeolite ZSM-5 using quasielastic neutron scattering (QENS) has shown that at low Si/Al ratios methanol rotates isotropically at room temperature, switching to diffusion confined to the channel intersections at higher temperatures.1 At high Si/Al ratios confined diffusion was observed at all temperatures, with higher 'mobile fractions' in the higher Si/Al ratio sample, illustrating the effect of a higher acid site concentration.

Our current work is focused on using MD simulations and QENS to characterise and quantify the behaviour of methanol within different CHA-type zeolite catalysts including SSZ-13 and SAPO-34. The different Si/Al ratios will allow us to probe the effect of increased acid site density on methanol mobility. QENS provides experimental self-diffusion coefficients and activation energies of diffusion on the nanoscale, and the average residence times associated with jump diffusion mechanisms common for sorbates in zeolite catalysts, all of which can be replicated by classical MD simulations. Upon reproducing the intermediate scattering function and elastic incoherent strcuture factor (EISF) from our atomic trajectories of methanol in SAPO-34 and SSZ-13 calculated from MD simulations, we have probed rotational motions. Models of isotropic methanol rotation was found to fit the MD-calculated EISF. We note that our simulations predict an increased level of mobility in the SAPO-34 catalyst at the displayed temperatures, with mobile fractions larger by roughly 15% in SAPO-34 compared to CHA. By varying Si/Al ratios in our ongoing simulations we can observed trends in mobility with varying composition, demonstrated previously in our simulations of methanol diffusion in H-ZSM-5.2 Direct comparison of QENS experiments with QENS observables extracted from MD may also allow for further parameterisation of forcefields used for classical simulations – creating more reliable simulations for further modelling of these catalytic systems.

1051 - UNIFYING SORPTION ISOTHERM FOR MICRO MESO AND MACROPOROUS MATERIALS

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A great pool of various theoretical adsorption isotherms is currently available for materials and process characterization. Most can be reduced to Langmuir, some to Polanyi's adsorption potential, newer ones, such as NLDFT based isotherms, mainly reflect the Lennard-Jones potential. The choice of the equation depends on the isotherm shape (type I-VI, IUPAC classification) and is often the outcome of tradition.

This contribution deals with the interpretation of high-resolution sorption isotherms by the formation of clusters. To understand cluster formation at surfaces, the basic idea is taken from the work of the biochemist Irvin Klotz describing the multiple adsorption equilibria of organic ligands on proteins [1]. The organic ligand may be replaced by N2, and the common picture of surface layers is now changed to clusters on a surface. The shape of the clusters is not defined, a multilayer may be seen as a special kind of (merged) clusters. Following the idea of Klotz, the loading of the adsorbent is mathematically given as a function of the relative pressure by a quotient of two power series containing individual thermodynamical equilibrium constants for each degree of clustering.

For adsorption in microporous materials the degree of clustering is limited by the maximal micropore filling, a process first described by Dubinin [2], while the individual equilibrium constants for different cluster sizes depend on the pore shape. Definite parameters are received by nonlinear regression towards a high-resolution experimental isotherm. Examples are presented concerning Ar adsorption in zeolites (type I) [3] for the first time.

Such a numerical determination of individual cluster equilibrium constants by nonlinear regression was found to be limited to maximal degrees of clustering below 20. Increasing cluster sizes require an additional general energy relationship with three parameters describing cluster formation on smooth or randomly corrugated surfaces. An example for that method is given by the analysis of ordered mesoporous materials with type IV isotherms. For relative pressures ranging from 10-6 to 0.95 and N2 and Ar sorption on MCM-41 [4,5], data are reproduced including capillary condensation [6]. The influence of hysteresis and mesopore width on the isotherm parameters is presented here for the first time.

Allowing infinite large clusters, the equations for mesopores can be simplified to describe adsorption in macropores without capillary condensation (type II) [6,7]. By splitting the set of equations to one perpendicular to the surface and another randomly oriented, it is possible to calculate surface areas [8]. They are smaller than those obtained by the BET model.

Several theoretical isotherms can be derived from the present general sorption model: These are the so-called zeta isotherm, the GAB, n-layer BET, and BET equation itself.

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1057 - ADSORPTION AND TRANSPORT IN ZEOLITIC MATERIALS

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Nanoporous materials such as zeolites, nanoporous carbons, and metal organic frameworks are at the heart of numerous important applications for our every day life : adsorption (gas sensing, drug delivery, chromatography), energy (hydrogen storage, fuel cells and batteries), environment (phase separation, water treatment, nuclear waste storage), Earth science (exchange between the soil and the atmosphere), etc. Among these materials, zeolites, which have pores $\lesssim$ nm, are particularly interesting as ultraconfinement in their porosity leads to novel adsorption and transport phenomena. In this talk, I will present how molecular simulation and theoretical approaches allow developing models on adsorption and transport in these extremely confining materials.1,2 I will first discuss the different adsorption regimes encountered when a fluid is set in contact with a porous material: from irreversible adsorption/capillary condensation for the largest pores to reversible/continuous filling for the smallest pores (such as in zeolites). We will see how simple thermodynamic modeling allows rationalizing these different regimes by considering reminiscent capillarity at vanishing lengthscales. Using Polanyi's adsorption potential theory, which is derived here from Hill's general scheme for adsorption, we provide a simple thermodynamic formalism to predict consistently adsorption both in the internal porosity and at the external surface of zeolites. While this seminal theory has been already applied for gases in nanoporous solids, its extension to describe both surface and volume adsorption is important to provide a general rational framework for fluid adsorption in finely divided materials. Then, we will show how transport in zeolites can be described without having to rely on macroscopic concepts such as hydrodynamics.3,4,5 Using parameters and coefficients available to experiments, we will see that transport coefficients can be rigorously obtained from simple models in the framework of Statistical Mechanics using models such as free volume theory and intermittent brownian motion. In particular, by combining neutron scattering experiments and molecular simulations, we propose a simple free volume theory to predict consistently diffusion in the internal porosity of zeolite solids. To demonstrate the applicability of this simple yet robust framework, we show that the free volume theory accurately captures diffusion in each direction of space but also when the molecular size of the adsorbate molecule is arbitrarily increased.

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1122 - ON THE NATURE OF EXTRAFRAMEWORK ALUMINUM AND BRONSTED ACID SITE INTERACTIONS IN A METHANOL TO HYDROCARBON CATALYST

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Synergistic interactions between Bronsted acid sites (BAS) and extraframework aluminum (EFAl) that alter the selectivity, activity, and lifetime of zeolites catalysts are receiving greater attention as a tuneable property. However, definitive knowledge regarding BAS-EFAl cooperativity remains elusive, largely stemming from ambiguity in EFAl identity and therefore active site structure. While EFAl is typically ascribed Lewis acidic character, the number of Lewis sites in zeolites does not correlate with the amount of EFAl, indicating that some, but not all EFAl species possess this character.[1] Clearly, EFAl speciation plays a critical role in catalyst function, but atomic-scale insight into the resultant active site structure is needed to identify its mechanistic impact and drive catalyst development. In this regard, theoretical efforts are critical for elucidating the structure of BAS-interacting EFAl and understanding how they alter reactivity in reactions like methanol-to-hydrocarbon conversions.

To clarify the chemical nature of EFAl species interacting with zeolitic active sites under catalytic operating conditions, this work performs a comprehensive screening of the charge and hydration states of key EFAl species at BAS in H-ZSM-5. Static molecular and periodic density functional theory (DFT) calculations disagree on which EFAl species is the most energetically or thermodynamically preferred. Hence, ab-initio molecular dynamics (AIMD) simulations were executed to monitor the stability and dynamic evolution of EFAl species in the vicinity of BAS under catalytic conditions. These robust simulations revealed two clear regimes of framework-bound and free EFAl species, both dominated by a tetrahedral [Al(OH)2]+ ion with either two bonds to the zeolitic scaffold or two water ligands, respectively. We find that free EFAl species do not achieve full octahedral coordination, and are likely not responsible for the octahedral aluminum ions identified through experimental characterization. More importantly, we observe that Bronsted acidic character is transferred from a BAS to its interacting EFAl under hydrated conditions.

The role of framework aluminium siting and density was tested in simulation cells containing multiple BAS in different configurations. Hydrogen bonding between EFAl species and the framework oxygens surrounding aluminum substitutions makes the position and coordination geometry of EFAl sensitive to BAS siting and density. Resultantly, the apparent acidity of BAS-EFAl complexes is also impacted. In addition to providing new insight into EFAl-modified active sites for future mechanistic studies to build from, this work exposes an opportunity to improve the behavior of EFAl-containing catalysts through the position of framework aluminum.

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1127 - ANALYSIS OF SORPTION ISOTHERMS OF ZEOLITES WITH THE EXCESS SURFACE WORK – THERMODYNAMICAL AND QUANTUM MECHANICAL DESCRIPTION

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The thermodynamic principles of excess surface work [1-3] and the combined approach with disjoining pressure [4] (ESW-DP) are well documented. The ESW model is also part of industrial patents. For modelling sorption isotherms, this ESW-DP approach is implemented in an extended version of the computational model for sorption isotherms and capillary condensation by Churaev, Starke, and Adolphs [5]. Thermodynamically, the excess surface work is defined as the sum of the surface free energy and the isothermal isobaric sorption work characterized by an energy minimum at the monolayer capacity. The basic idea of the ESW-DP model is that during adsorption on the pore walls, the approaching films collapse, and capillary condensation occurs. Evaporation is described by a modified Kelvin equation. It has been shown that one solution to the ESW equation is the double log linear representation of the change in chemical potential as a function of the amount adsorbed. This is also known as the De Boer-Zwicker equation from 1929 [6]. Brunauer, Emmett, and Teller [7] mentioned the linear behaviour of this equation but could not find an explanation. A quantum mechanical approach using perturbation theory was used in the χ-equation of J. B. Condon [8]. Again, this χ-equation is essentially the same as the De Boer-Zwicker equation. Therefore, the ESW approach can be explained not only thermodynamically but also quantum mechanically.

Applications are presented on zeolites MCM 41, MCM 36 and SBA 15. The ESW-DP can be used to simulate the entire isotherm with its specific hysteresis. Furthermore, it is possible to calculate specific surfaces such as BET using the ESW method (9-11), in addition to real sorption energies and pore size distributions. Comparisons to NLDFT calculations with argon and nitrogen are shown. NLDFT simulations of water vapor sorption is not yet possible, but with ESW-DP. Water vapor sorption on hydrophilic and hydrophobic surfaces can be described in more detail with the χ-equation and the linear solution of ESW (de Boer-Zwicker equation), respectively [12]. A reference isotherm is not necessary at all.

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1140 - DFT MODELLING OF CATALYTIC TRANSFORMATIONS OF ADSORBED SPECIES IN ZEOLITE SYSTEMS

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Zeolites are used as catalysts for various chemical reactions that take place in their channels or cavities. The catalytic role of zeolites is due to bridging OH groups and/or extra-framework metal cations, which represent Brønsted (H+) [1] and Lewis (Men+) acidic centers, respectively. Combining IR and DFT results we demonstrated that when CO interacts with Brønsted acid sites in H-MOR zeolite super-electrophilic HCO+ cation can be formed. Such species are catalytically active in the conversion of dimethyl ether and hydrocarbons to methyl acetate and aldehydes.

In another combined experimental and theoretical study we found that CO can be oxidized to CO2 at very low temperature, -140^{o}C, by a non-metallic catalyst - HNO3 molecule located in a protonated form of chabazite [3]. We have clarified the detailed mechanism of the process and encountered that the initial CO interaction with the Brønsted acid zeolite proton is crucial. It leads to a formation of an -H+-CO complex which facilitates the nucleophilic attack of an O center from the nitrate to the carbon atom from CO. Combining spectroscopic, catalytic, and DFT studies we also showed that nitrosyl cations (NO+) located in the pores of chabazite are the key intermediates for selective catalytic reduction [4]. They have been found to react with ammonia even below room temperature as N2 and H2O are produced. Interestingly, no copper cations are required for N2 formation. We modeled two pathways for the NO reduction reaction with NH3 on zeolite/NO+ catalyst: with and without the direct participation of the substrate. The calculated barriers were very low (below 20 kJ/mol) when the zeolite substrate participates in the reaction, manifesting that the reaction can occur at very low temperatures as predicted by the experimental data. We suggested that nitrosamine (NH2NO) and NNH+ species can be formed as intermediates.

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1145 - TRACKING LIGHT OLEFIN DIFFUSION IN ZEOLITE MFI VIA MACHINE LEARNING TECHNIQUES

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The methanol-to-olefins (MTO) conversion on acid zeolites has emerged as a promising step in the production of chemicals from alternative carbon feedstocks such as biomass or captured CO2. The MTO product selectivity is typically governed by a complex interplay of the competition between multiple catalytic reaction cycles, the stabilisation of key intermediates, and transport phenomena. [1-3] The shape selective topology of the confined zeolite may impose a significant impact on the diffusivity of guest molecules. Depending on the loading, the presence of deactivating species and the zeolite acidity, hydrocarbon diffusion may occur freely or become hindered. [4] In MTO conversion, the zeolite micropores host a complex reaction environment including both oxygenate species as well as hydrocarbon pool compounds. Consequently, the catalyst loading evolves dynamically and diffusion limitations may show a significant correlation with the ultimate product selectivity. [5] A proper understanding of the relationship between diffusivity and the zeolite structure, acidity and loading is essential to improve the catalytic performance and lifetime of zeolites. Nevertheless, the precise effect of acidity and pore occupation by guest molecules on the diffusion of light olefins remains unresolved to date.

In this contribution, we present a novel computational approach to characterize light olefin transport in zeolite MFI, a common MTO catalyst. More specifically, we assess whether diffusion occurs isotropically in all directions and whether the presence of Brønsted acid sites and guest molecules (e.g. aromatics) plays a role in the microporous transport. To this end, ab initio molecular dynamics (MD) simulations are performed to track the diffusion of a single molecule at operando conditions. Subsequently, our ab initio data are used to train a machine learning potential (MLP) which is employed to perform MD simulations at longer length and time scales in order to reliably estimate diffusion coefficients. A properly trained MLP can reproduce all host-guest interactions with high accuracy at a significantly reduced computational cost, thus allowing to screen diffusion properties in a broad set of materials with varying acid site distributions and guest loadings. Our computational observations are complemented by pulse-response TAP measurements and PFG-NMR spectroscopy to probe external surface interactions and internal pore diffusion.

First, we explore the feasibility of different diffusion pathways through the interconnected straight and sinusoidal 10-ring channels of zeolite MFI in the absence of acid sites. Olefins preferentially reside at channel intersections and may sporadically travel to adjacent intersections. It is demonstrated that the specific pore architecture results in diffusion anisotropy with the straight channel pathway being slightly preferred over the sinusoidal pathway. Secondly, the influence of the acid site density is addressed. Our results reveal that the presence of Brønsted acid sites on the 10-ring channels has a clear promotional effect on light olefin diffusion. Thanks to the favourable formation of π-H interactions and the potential formation of carbenium ions upon protonation, alkenes can travel faster through the zeolite pores. Also the distribution of the acid sites inside the channels or located at the intersections is found to play a crucial role. The computational trends uncovered by our MLP-MD simulations may lead to the synthesis of zeolites with dedicated acid site distributions to promote or impede the transport of alkenes, opening up new perspectives for tuning the catalytic selectivity or for separation purposes.

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1157 - ACTIVATION BARRIER FOR BENZENE METHYLATION WITH METHANE LOWERED BY STRONG BENZENE ADSORPTION

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We found unique catalytic activity of Co/MFI zeolite for methylation of benzene with methane [1]. Even apart from a potential for production of a part of chemicals from methane, driving force of the reaction between the inert reactants (methane and benzene) is an interesting research subject. Here the reaction mechanism is analyzed to show unique feature and the origin of catalytic activity of for methane activation and the reaction.

The first-principles calculation shows that, on α-type [2] Co2+···(AlO2)2−(SiO2)94, where (AlO2)2−(SiO2)94 shows MFI framework with 0.74 nm of the Al-Al distance, the methylation of benzene with methane proceeds. Benzene is adsorbed on Co2+ with evolving 143 kJ mol−1 of the adsorption heat. After methane adsorption, the energy level of Co2+(C6H6)(CH4)···(AlO2)2−(SiO2)94 reaches to the energy level of −170 kJ mol−1 compared to the start of reaction (free active site, benzene and methane). Then, the reaction needs passing 166 kJ mol−1 barrier for methane cleavage into Co+(C6H6)(CH3)···(AlO2)−(AlO2H)(SiO2)94; the energy level of its transition state was −4 [= 166−(−170)] kJ mol−1, indicating easiness of methane activation assisted by benzene adsorption. In contrast, in the absence of benzene, methane cleavage needs to overcome a 141 kJ mol−1 transition state. Following benzene ring methylation step to get Co+(C6H6-CH3)···(AlO2)−(AlO2H)(SiO2)94 is the rate-determining step with the highest energy level of 76 kJ mol−1, close to the experimentally observed activation energy of reaction. These indicate that the strong adsorption of benzene offsets the high activation barrier for the methane activation, and this is the driving force of the catalytic reaction. The mechanism under strong adsorption of benzene is in agreement with experimentally observed kinetics.

Difference in the microstructure of active site significantly affects the energy diagram. β-type Co2+ [2] cannot adsorb benzene due to steric hindrance, because the β-type Co2+ is buried in a plane consisting of four framework oxygen atoms, while α-type sticks out into channel. Experiments with varying Co ion exchange extent and co-existing elements indicated the high activity of α-type Co species [3], and further, use of MEL framework with enriched α-positions resulted in high activity [4]. Even on α-type, slightly short or long Al-Al distance gives significantly high activation energy. The former is because of too strong Co-O bond, while the latter is due to the difficulty in acceptance of H+. These also agree with experiments where the activity showed a volcano-shape relationship against framework Al concentration, and 0.3 mol kg−1 of the concentration (framework Si/Al molar ratio = 50) gave the maximum activity.

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1253 - ORGANIC AND INORGANIC STRUCTURE DIRECTING AGENTS IN THE SYNTHESIS OF ZEOLITES.

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It is well known that organic and inorganic structure directing agents (SDA) play an important role that contributes to drive the synthesis towards energetically favoured specific zeolite phases [1]. Of these, organic SDAs (OSDAs) are particularly important since their energetic contribution is not only considerably strong (through short-range intermolecular interactions, aka zeo-OSDAvdW) but also their role can be easily rationalised in terms of shape-selectivity, this meaning a sort of match between the respective shapes of OSDA and zeolite micropore. This importance is reflected in the fact that synthesis teams often try to generate new OSDAs as a strategy to synthesise new zeolites, although this is of course not the only way. Recently a number of computational groups have applied the availability of databases (of both zeolites and OSDAs) with different algorithms to generate the corresponding zeo-OSDA pairs and estimate their zeo-OSDAvdW energies as well as to analyse structural and chemical descriptors in order to estimate zeolite feasibility [2-5].

zeoTsda software allows to automatically fill OSDA molecules inside pure silica zeolites and find the maximum loading [3], in good agreement with experimental loading. This only needs an XYZ file for the OSDA molecule as well as the CIF file for the zeolite, and it runs across both databases of zeolites and OSDAs. zeoTsda software has recently been employed to find new candidate OSDAs for ITE zeolite [6] and to explain the directing role of fluoride anions in the syhthesis of zeolites [7]. The synthesis of different pure silica zeolite phases using the same OSDA in the presence and absence of fluoride allows to calculate the energetic stability on each case and establish which synthesised zeolite phase is most stable. The calculated results are in agreement with experiments.

Recently we have added zeoTAl, initially employed to calculate Al distributions in zeolites [8], to our library of zeolite synthesis software packages. This now allows to extend calculations to Al-containing zeolites and calculate energies of zeo-OSDA unit cells with full OSDA loading. Al contents are considered so as to counteract the positive charge of all the OSDAs in the unit cell, and Al distribution is chosen as the most stable from those generated by zeoTAl. Additionally, a new general equation (for zeolites in all the compositional range 0 ≤ Al/(Si+Al) ≤ ½) has been introduced, that allows to assess zeolite stability [9].

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1254 - COMPUTATIONAL MODELING OF ACIDITY AND SPECTRA OF HYDROXYL GROUPS IN ZEOLITES

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Computational modeling based on density functional calculations was used to contribute in the interpretation of experimental spectral features and acidity of hydroxyl groups in zeolites as well as the interplay between silanols and bridging hydroxyls. The calculated 1H NMR chemical shifts of both silanols and Brønsted acid sites (BAS) were found to correlate linearly with the stretching O-H vibrational frequencies of the individual O-H groups as well as with the corresponding O-H bond length [1,2], as suggested earlier on the base of experimental measurements [3]. From the correlations we derived corresponding coefficients that allow to determine the frequency value from NMR shift and vice versa. The correlation of those spectral characteristics with the hydrogen bond length is more complex and allowed us to differentiate several groups of silanols based on their participation in hydrogen bonds: (i) isolated silanols; (ii) proton-acceptor silanols; (iii) proton-donor silanols in weak hydrogen bonds; (iv) medium hydrogen bonded silanols; and (v) strong hydrogen bonded silanols. The calculations suggested that the flexibility of the silicon tetrahedron at which the proton-donating and proton-accepting silanols are bound is the main factor determining the formation and strength of the hydrogen bonds, and subsequently its spectral features.

As an estimate of the acidity of bridging hydroxyl groups and silanols we calculated their deprotonation energies. Comparison of those energies with the spectral characteristics of the same hydroxyl group, showed that lack of any correlation. Further, using the calculated deprotonation energies of silanols and BAS in zeolite models and available experimental values for deprotonation enthalpies of small acid molecules in the gas phase we derived estimate for real deprotonation energies values of the hydroxyl groups in zeolites. This allowed us to address the long-standing question of the acidity of the zeolite acid sites with respect to the well-known acidic compounds as nitric acid, sulfuric acid, and super acids. With the obtained enthalpy values we positioned properly BAS and silanols in zeolites into the general scale of gas phase acidity - the BAS sites in zeolites fall in the range of super acids while silanols cover wide range from strong acids to super acids [2].

We also modeled defect sites in periodic USY zeolite framework, created during steaming of the parent material. The goal of this simulation was to assist in clarification of the experimentally observed accessibility of hidden bridging hydroxyls inside the sodalite cage for reactants and basic probe molecules [4]. The calculations suggested that direct interaction of BAS in the sodalite cage with the probe molecule cannot occur due to repulsion from silanols forming silanol nest. However, those silanols act as mediators of the proton transfer as they protonate the guest molecule and after that they are restored via proton transfer from BAS in the sodalite cage.

The calculations of the IR and NMR spectral features of silanols and bridging hydroxyls were performed for zeolite nanoparticles models with ORCA code using DFT method with hybrid exchange-correlation functional PBE0. The periodic DFT calculations were done with VASP code using PBE functional.

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1276 - THEORETICAL MODELING OF PATHWAYS FOR THE TRANSFORMATION OF FRUCTOSE AND XYLOSE TO CARBOXYLIC ACIDS OVER NA BEA ZEOLITE.

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The purpose of the process is to develop a method for obtaining C1–C5 carboxylic acids (levulinic acid, oxalic acid, lactic acid, and formic acid) from a mixture of C6 and C5 carbohydrates derived from waste lignocellulosic biomass – hemicellulosic fraction is essential for industry [1-3]. However, understanding mechanism of those processes will bring essential knowledge to better plan zeolite architecture. Theoretical modeling involved understanding the changes that occur during the conversion of xylose and fructose to levulinic (LE), lactic (LA), oxalic (OA) and formic acids (FA) proceeding in the presence of an Na-BEA zeolite.

The electronic structures of BEA zeolitewere calculated using ab initio density functional theory (DFT) methods (program StoBe) with the non-local generalized gradient corrected functionals according to Perdew, Burke, and Ernzerhof (RPBE), in order to account for electron exchange and correlation. Cluster models of beta zeolite (hierarchical zeolite: $Al_2Si_{12}O_{39}H_{22}$ and ideal pore $Al_2Si_{22}O_{64}H_{32}$) have been used with Na ion above aluminium centers in the zeolite frame.

Modeling included the conversion of fructose and xylose to levulinic, lactic, oxalic and formic acids with Na-BEA. The several paths of fructose and xylose to carboxylic acid have been considered (Figure 1), which involves the steps of protonation/deprotonation, hydration/dehydration and oxidation reactions.

1281 - DYNAMICS OF [CU(NH3)2]+ SPECIES IN CU CHA CATALYSTS FROM MACHINE LEARNING DRIVEN ATOMISTIC SIMULATIONS

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Cu-exchanged zeolites play a crucial role in the chemical industry as redox catalysts. In particular, the small pore Cu-CHA is employed in the abatement of NOx emissions with the selective catalytic reduction (SCR) using NH3 as reductant. [1] Interestingly, in this reaction the active sites, Cu+ and Cu2+cations, are not purely heterogenous. These cations can suffer important changes in their local environment because of their interaction with guest molecules. At low temperature (< 523 K), NH3 mobilizes the Cu+ cations forming [Cu(NH3)2]+ complexes that participate in the activation of O2. The diffusion of the monomeric [Cu(NH3)2]+ species to the adjacent cage through the 8r window is the rate-determining step at low Cu loading (10-4 Cu/Å3). This diffusion is limited because of the electrostatic interactions with the zeolite framework, and thus constitutes an intermediate situation between homogeneous and heterogeneous catalysis. [2] Despite its relevance in the NH3-SCR the diffusion of Cu cations within zeolites is still under-investigated. The theoretical study of these systems requires either long DFT based molecular dynamics simulations or enhanced sampling techniques which are extremely expensive computationally. In recent years, machine learning potentials (MLPs) have gained special relevance in the areas of materials science and heterogeneous catalysis, because they can make predictions with the accuracy of quantum chemistry methods and with speeds orders of magnitude greater. [3]

In this contribution, we develop a neural network potential that allows breaking the picosecond scale accessible with regular AIMD and allows the simulation of systems with thousands of atoms which is impractical using only DFT. We address two important questions regarding the dynamics of the Cu+ cations in Cu-CHA. The first one, related to short-range diffusion, is how the Al distribution impacts the diffusion of diaminecopper(I) between neighboring cages. We have found that, in general, Al pairs in 8R are beneficial for the diffusion by lowering the free energy of activation by 1.8 kcal/mol and stabilizing two diamine-copper(I) complexes in the same cage. These results show that the rate of the SCR can be accelerated almost two orders of magnitude by selectively positioning the Al atoms as Al pairs, in the 8R. We also observe that the formation of complex pairs inside the Cu-CHA increases at higher Cu content and at low Si/Al ratios. The second question, related to long-range diffusion, is how far the diamine-copper(I) complexes can travel inside the CHA. Our simulations show that at 500 K these species can visit on average more than 3 cages and diffuse as far as at least 30 Å in a few nanoseconds for systems with Si/Al = 30 and lower. This distance does not appear to be limited by the mobility of NH4+.

Our results demonstrate the power of combining high-throughput DFT calculations with machine learning and establishes the importance of using MLPs to gain more useful insights from more realistic models.

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1298 - HOW TO DETERMINE THE INTRINSIC BRØNSTED ACIDITY OF ALUMINOSILICATE ZEOLITES

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The Brønsted acidity strength of aluminosilicate zeolites is a topic that has not been fully resolved, although numerous experimental and theoretical studies were conducted often with contradictory observations. The definition of Brønsted acidity is its willingness to donate a proton inevitably leads to a computational abstraction of deprotonation energy (DPE), which can easily scale the acidity strength of different sites and topologies of aluminosilicate zeolites. This concept was proposed to remove the necessity of adsorption of probe base molecules, which have shown quite inconclusive results. On the other hand, the DPE describes a very artificial process that does not resemble the realistic deprotonation process due to the base absence. Furthermore, the correlation between base adsorption heats and DPE values is not observed and even expected. In this work, the main focus was to determine the intrinsic Brønsted acidity of aluminosilicate zeolites with high Si/Al ratio through adsorption of base probe molecules of increasing proton affinity (acetonitrile, acetone, formamide, ammonia). The main conclusions can be summarized as follows: (i) the degree of BAS deprotonation can be monitored via deformation of AlO4 tetrahedra and this provides significantly better descriptor that just proton distance from the zeolitic oxygen , (ii) in case of strong bases such as ammonia and formamide the site is deprotonated, and thus the information about the site acidity is not accessible and corresponding adsorption energies do not correlate with DPEs, (iii) the formamide is not an optimal probe due to the formation of two strong hydrogen bonds to the oxygens connected to Al and thus appears more acidic than it would correspond to its proton affinity, (iv) there is clear correlation in degree of deprotonation between acetone and acetonitrile indicating high consistency with how the probes sense the zeolite acidity and acid strength of BAS can be scaled accordingly and (v) experimental verification of these observations is hardly accessible due to the very small differences between the materials or even sites within the materials themselves.

1327 - LOCAL AND NANOSCALE WATER BEHAVIOUR IN ACIDIC ZEOLITE CATALYSTS

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Water behaviour in zeolite catalysts has significant implications for the catalytic properties of the material [1]. As such, the effect of zeolite composition (in particular the Si/Al ratio) on the behaviour of water is of great interest to these applications. The combination of quasielastic neutron scattering (QENS) and classical molecular dynamics (MD) simulations is particularly powerful for probing the nature/rate of adsorbate dynamics in zeolite catalysts across a range of lengthscales – from rapid local motions close to the active site, through to the longer range nanoscale diffusion through the framework. Our studies combine these techniques to gain a detailed qualitative/quantitative understanding of water dynamics local to the active site (rotations/confined translations) and longer range diffusion through the framework as a function of Si/Al ratio (i.e. acid site density) in important commercial catalysts H-ZSM-5[2] and HY.

The QENS experiments probed 3 commercial H-ZSM-5 samples with Si/Al ratios of 15, 40 and 140 (Zeolyst international), at water loadings of ~3 wt%. HY samples with Si/Al ratios of 2.6, 15 and 40 were sourced from Fischer Scientific and probed water diffusion at a loading of ~18 wt%. QENS measurements of water diffusion in H-ZSM-5 and HY employed the OSIRIS spectrometer at the ISIS neutron source and the IN5 spectrometer at the ILL respectively. MD simulations employed the DLPOLY4 code to model atomic trajectories over several nanoseconds, where long range diffusion coefficients were calculated, but also the trajectories were sampled over the time windows observed by each spectrometer, and QENS observables (EISF, and line broadenings) were then directly reproduced from the simulation.

QENS studies of water in HY showed that water undergoes diffusion confined to the FAU supercage (12 Å diameter), and also rotates isotropically at all 3 Si/Al ratios. Confined diffusion gave diffusivities of 0.6 – 1.1 × 10-9 m2s-1 showing a positive correlation with the Si/Al ratio. The rotational diffusion coefficients ranged from 1 - 1.75 × 1011 s-1 and were consistent across all Si/Al ratios. Qualitative agreement was found with the MD simulations which showed water diffusion confined to FAU supercages, as well as isotropic water rotation with rates modelled within experimental error.

In H-ZSM-5 [2], the QENS experiments showed water diffusion was confined to a sphere with radii ranging from ~3.5-4 Å, suggesting the mobile water was located within the MFI channel intersections, giving localised diffusion coefficients in the range of ∼1–2 × 10−9 m2s−1. In the Si/Al = 140 ZSM-5 sample, diffusion was observed to be less confined and longer range in nature, with higher diffusivities (∼1-5 × 10−9 m2s−1) (fig 1.a). MD simulations observed a reduction to the Ds by a factor of 2 from a fully siliceous MFI system to that with Si/Al = 15 (fig 1.b), due to the strong coordination and increased water residence time at acid sites (fig 1.c). QENS observables, both the elastic incoherent structure factor (EISF) and quasielastic line broadenings, were reproduced from the MD trajectories giving qualitative and quantitative agreement with experiment. The MD calculated EISF showed the experimentally observed diffusion confined to a sphere (radii 3.5 - 6 Å) was also present in our simulations, with Ds values calculated within experimental error.

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1337 - THE ROLE OF ALKALI CATIONS IN PRECURSOR LIQUIDS FOR ZEOLITE FORMATION THE CASE OF HYDRATED SILICATE IONIC LIQUIDS

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Although zeolites are very important for many industries, their formation is still not fully understood due to the difficult experimental conditions in which formation occurs. On the other hand, theoretical models have been hampered by the troublesome modeling of hydrogen bonds present in the crucial water solvent. Recently, a new synthesis route was proposed whereby the main problems (pressure build-up and gel-formation) for direct observation and characterization are evaded. Hydrated silicate ionic liquids (HSILs), are fully clear and contain no particles or gel-phases and a very limited number of water molecules. Furthermore, it was found that the formation of zeolites is triggered by aluminum addition, allowing a very controlled propagation of the formation process. Since then, HSILs have been under intense experimental investigation in order to characterize the ionic liquid, assess the role of aluminum (needed to start zeolite formation) and construct a generally valid model for zeolite crystallization.

Given the low amount of water, the presence of only small molecular (alumino)silica species (monomers, dimers, 3- and 4-rings) and the fact that formation only starts upon introduction of low amounts of aluminum, accurate molecular modeling of these systems also becomes feasible. This is important as it is widely known that the topology of the zeolite is governed by the cations present in the synthesis medium. As such, accurate modeling of HSIL is expected to give important insights into the structure directing effects of the synthesis conditions towards the final zeolite topology. In this work, a simple molecular model is developed to study the behavior of HSIL liquids prior to nucleation, to elucidate the role of the alkali cations (sodium, potassium, rubidium and cesium) prior to nucleation.

To this end, molecular dynamics simulations were performed showing that the behavior of the liquid is governed by an interplay between ion pairing and diffusion that is strongly dependent on the charge density and concentration of the alkali cation. Furthermore, a detailed molecular picture shows that the cation is capable of bringing several silicate monomers together in perfect orientations for condensation reactions that underlie zeolite formation. The theoretical results are validated by experimental measurements on similar model HSIL systems.

1036 - EXPERIMENTAL DETERMINATION OF CHARACTERISTIC CURVES OF ZEOLITES WITH A HYDROTHERMAL STABILITY TEST SETUP

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Thermal energy storage based on adsorption and desorption of water on adsorbents promises high energy storage densities. Zeolites are well-known adsorbents and those with high water adsorption capacities are potentially interesting for application in thermal energy storage systems. The so-called characteristic curve of an adsorbent links the adsorbed water volume to the adsorption potential. With a characteristic curve available, the adsorption potential and, hence, the heat of adsorption of an adsorbent can be calculated for different conditions encountered in specific applications. Thus, the maximum storable amount of thermal energy can be assessed at a material level. However, it is notoriously difficult to obtain the required equilibrium data over a large range of sample temperatures and dew point temperatures.

At ZAE Bayern, a multiple sample setup was built to test the hydrothermal stability of adsorbents. The setup has 4 temperature-controlled sample blocks, each containing 4 sample containers. 4 sample containers of each sample block are connected orthogonally to each other and to 1 of 4 temperate water reservoirs. With this configuration, samples can be exposed to a total of 16 different conditions of temperature and dew point through setting 4 different temperatures and 4 different dew point temperatures. Thereby, the temperature range of each sample block is between 30 °C and 350 °C, while that of each water reservoir is between 5 °C and 70 °C. Due to these wide ranges, the existing test setup has potential to acquire the equilibrium data for the construction of characteristic curves. The aim of this work is thus to check the feasibility.

Two well-known zeolites were measured: 13XBFK and NaYBFK, both binder-free and from Chemiewerke Bad Köstritz GmbH (CWK). Even though it is possible to obtain 16 data points with one measurement run, it proved to be impractical due to the large required ranges of sample temperatures and dew point temperatures. Therefore, and to avoid ageing of the samples, a different strategy was adopted for the measurements. The samples are first dried in different stages up to a temperature of 350 °C for around 20 hours and under constant evacuation of the sample containers. Subsequently, the samples are subjected to 4 different sample temperatures and 2 different dew points for 24 hours. Thus, for these 8 conditions, 8 data points are determined for the construction of a characteristic curve. In order to obtain a total of 24 data points, the whole procedure including the drying process is repeated two times with a different set of sample and dew point temperatures. Each one of the 24 data points is the arithmetic mean value of the results obtained for 2 samples. Hence, the data points become more reliable and outliers can be more easily determined, while the downside is a longer measurement time.

For both zeolites, characteristic curves were determined for an adsorption potential (DF) between 81 kJ kg-1 ≤ DF ≤ 2192 kJ kg-1. The determined characteristic curve for CWK 13XBFK is valid for an adsorbed water volume (Wads) between 0.030 cm3 g-1 ≤ Wads ≤ 0.336 cm3 g-1. For CWK NaYBFK the validity is between 0.009 cm3 g-1 ≤ Wads ≤ 0.323 cm3 g-1. Both characteristic curves are in good agreement with existing ones determined with other measurement devices. It was thus shown, that it is possible to determine characteristic curves for the two tested zeolites with the existing hydrothermal stability test setup.

1092 - ACTIVATION OF MOLECULAR OXYGEN OVER FE FER AND FE *BEA ZEOLITES

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Direct application of molecular oxygen for the transformation of hydrocarbons into value-added oxygenates, being a platform for chemicals and energy vectors, is of paramount importance for sustainable catalysis. Very recently, it was shown that the binuclear iron sites in FER zeolite exhibit exceptional ability to split O2 into active oxygen (α-O) species, able to oxidize methane already at room temperature with the spontaneous release of the reaction products, methanol, and carbon dioxide to the gas phase [1]. DFT calculation predicted that those unique active sites could also be formed in other zeolitic topologies possessing proper geometrical arrangement of cationic sites and a high fraction of Al pairs (Al-O-Si-O-Al sequences in one ring) [2]. Among them, wide-pore *BEA topology draws our attention as it possesses enhanced transport properties and can be synthesized with a low Si/Al ratio [3]. The aim of this work is not only verification of the DFT results concerning the formation of binuclear iron sites in zeolites of *BEA topology but also a comparison of the redox behavior of those centers in *BEA and FER during their oxidation by O2 studied by in-situ XAS and Mössbauer spectroscopies, and subsequent interaction with methane as a testing reaction. Commercially supplied FER (Tosoh Corporation, Si/Al 8.5) and synthesized in-lab Al-rich *BEA (Si/Al 4.5) [3] with a high population of Al-pairs were transferred into NH4-form and impregnated with acetylacetonate solution of FeCl3. Iron speciation and its redox properties were investigated in Fe-FER and Fe-*BEA with the use of in-situ Mössbauer and XAS spectroscopies during (i) evacuation of the samples at 450 °C, (ii) their interaction with O2 and (iii) subsequent reaction with CH4 with both steps, (ii) and (iii) carried at temperatures ranging from RT to 220 °C. Splitting of O2 and the formation of α-O over studied samples at various temperatures were investigated in activity tests towards methane oxidation with the FTIR and mass spectrometry (MS) detection of the reaction products. Mössbauer and XAS spectral characteristics of evacuated Fe-FER and Fe-*BEA (Fe/Al < 0.1) confirmed the presence of atomically dispersed Fe(II) cations. Interaction of both samples with O2 reveals significant differences, indicating the higher activity of binuclear iron sites in Fe-FER towards the formation of α-O already at RT. Nevertheless, obtained results proved the splitting of O2 also over Fe-*BEA at higher temperatures, which is reflected in spectra by the changes of both the oxidation state and geometry of the iron sites. In-situ XAS spectra registered after the interaction of α-O formed over Fe-FER and Fe-*BEA with methane confirmed that the redox cycle occurred and active sites were restored. Activity tests with FTIR and MS detection revealed the presence of methanol and CO2 directly in the gas stream with a better catalytic performance of Fe-FER at a lower temperature range in contrast to Fe-*BEA, showing higher activity above 160 °C. Yet, both samples were stable in three consecutive redox cycles. Manifested discrepancies in the activity of binuclear iron sites in FER and *BEA are in line with a higher energy barrier of the O2 splitting over Fe-*BEA.

The presented study proved the splitting of O2 over binuclear iron centers in zeolites other than FER and shed light on structural-functional relations in the activation of O2, which might be pronounced in its further utilization in the oxidation of hydrocarbons.

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1137 - WHICH SPECIES DEACTIVATE THE CATALYST IN MDA REACTION MOLYBDENUM AND OR COKE

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Methane dehydroaromatization (MDA: $6\ CH_4 \leftrightharpoons C_6H_6 + 9\ H_2$) under non-oxidative conditions over the singular Mo/HZSM-5 bifunctional catalyst has arisen as a key technology to upgrade methane into simultaneously CO_2 free energy vector and building-block chemical intermediates1. Yet, the limited single-pass thermodynamic equilibrium into benzene (~ 12.5 % at 700 °C) and the rapid catalyst deactivation by coking favored at high temperatures hinder the potential industrialization of the process. MDA benchmark catalyst made of molybdenum, generally impregnated on a protonic HZSM-5 zeolite, is known to evolve permanently from pre-treatment to deactivation. During the calcination, the initially deposited molybdenum active site precursors on a protonic zeolite migrated toward Brønsted acid sites[2]. Then, their reduction into carbide centers initiate the production of aromatic compounds resulting in coke deposition on the catalyst. The latter is principally responsible for catalyst deactivation[3]. A detailed ex-situ kinetics study was carried out in methane dehydroaromatization over three different Mo-loaded bifunctional Mo/HZSM-5 catalysts: 0.9 wt.%, 2.7 wt.%, and 17.2 wt. % Mo. This investigation has revealed two main deactivation modes: (i) irreversible damage due to the zeolite amorphization occurring during the inert isothermal pre-treatment, (ii) reversible deactivation by coke deposition (“soft”, “hard” and carbide species). The former principally occurs for high Mo-loaded samples leading to poor catalytic activity.

The catalysts presenting a well-balanced Mo loading suffer mainly from the second deactivation mode. The catalyst decay could be modeled according to semi-empirical laws as a function of time on stream and coke amount. The latter led to catalyst textural and structural modifications possibly connected to the loss of catalytic activity. Two deactivation descriptors of the aged catalysts and one descriptor of the deactivating species were identified: (i) coke amount recovered on the spent samples, (ii) loss of microporous volume, and (iii) monoclinic/orthorhombic phase transition of the HZSM-5 zeolite, respectively. Further characterization of the deactivating species shed to light that both molybdenum and carbon species were responsible for catalytic deactivation for well-balanced catalysts. At least 50% of the initially dispersed molybdenum moieties migrated toward the external surface to form large clusters of molybdenum carbide. The use of coke extraction allowed to determine the exact chemical nature of coke species trapped inside the zeolite channels. They were mainly constituted of unsubstituted polyaromatic compounds driven by the zeolite internal framework.

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1139 - TUNING HYDROCRACKING PROCESS PARAMETERS

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Gas-to-Liquids (GTL) and Coal-to-Liquids (CTL) processing are attractive routes for the production of clean liquid transportation fuels, in particular middle distillate fuels, as an alternative to crude oil refining (provided the CO2 released in CTL is captured and utilised). The industrially proven and economically viable route starts with conversion of coal or gas to synthesis gas (syngas; a mixture of CO and H2) followed by Fischer-Tropsch synthesis (FTS) to hydrocarbons and subsequent product workup, as the FTS is notoriously unselective - producing a product stream with a very wide hydrocarbon chain length distribution. In practice, FTS is being developed towards long hydrocarbon chain (wax) production - followed by hydrocracking to obtain a high yield of transportation fuels.

Hydrocracking of FTS wax (dewaxing) is generally performed using a bifunctional catalyst, containing a hydrogenation/dehydrogenation function and an acidic function. The presentation will focus on Pt noble metal (de)hydrogenation / zeolite solid acid catalysts.

Two approaches have been studied to improve the yield of transportation fuels in the dewaxing process. One focusses on the synthesis of zeolites with hierarchical pore systems, introducing mesopores next to the inherent micropores. This serves to decrease diffusion limitations and especially the secondary cracking that results from long residence time in the zeolite pores. The other focusses on process parameters. We have studied the presence of water in the feed and the total process pressure. Water is the main byproduct of FTS, and leaving it in the feed stream to the dewaxing step allowed evaluation of the integration of synthesis and hydroprocessing for the potential single-train production of middle distillates with good cold flow properties. We found HC catalysts to be incompatible with the presence of CO in the feed, and the presence of water to decrease the activity and increase the selectivity to linear products - both due to competitive adsorption on the acid sites [1]. Surprisingly, when using zeolites as solid acids, we find that lowering the total process pressure to atmospheric increases the diesel yield dramatically. This makes the whole process much more economical in terms of CAPEX and energy efficient in terms of OPEX and CO2 footprint [2]. This is in contradiction to previously reported results using amorphous silica-alumina (ASA) as a solid acid, where more diesel is formed at higher pressure [3,4].

The gas used to produce the syngas can be biogas produced from organic waste, making the resulting transportation fuels sustainable and greenhouse-gas-free.

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1141 - HIGH PRESSURE INTRUSION OF SODIUM PERCHLORATE AQUEOUS SOLUTIONS IN PURE SILICA ZEOLITES STRUCTURE DEPENDENT NEGATIVE OSMOTIC EFFECT

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Heterogeneous lyophobic systems, which combine a lyophobic porous matrix and a non-wetting liquid, are one of the promising technologies to absorb and store the mechanical energy. Since 2001, high pressure intrusion of water in hydrophobic pure silica zeolites (zeosils) has been studying for these applications [1]. Depending on zeolite structure, framework stability and presence of defects, the “zeosil-water” system is able to restore, dissipate or absorb the supplied mechanical energy and therefore to display a spring, shock-absorber or bumper behaviour. Later, it was found that the use of aqueous salt solutions could considerably improve the energetic performances of such systems by a strong increase of intrusion pressure with salt concentration [2] that is attributed to osmotic phenomena as well as to distortion and dehydration of solvated ions under penetration into the pores. In some cases, the behaviour of “zeosil – solution” systems changes when highly concentrated solutions are used [3]. Recently, it was discovered that the nature of anion had a drastic influence on the behaviour of the systems [4], but its influence on intrusion pressure values was also pronounced. Nevertheless, for all the salt solutions and all the zeosils studied, intrusion pressure is higher than the one for water and it increases with salt concentration.

However, it has been observed that the intrusion pressure of aqueous solutions of sodium perchlorate is lower than the water one (96 MPa) in MFI-type zeosil (3D channels with 10 MR pore openings). For the most concentrated solution with H2O/NaClO4 molar ratio of 3.5, the intrusion pressure is 71 MPa. Moreover, it increases with solution dilution and equalize with the water one at H2O/NaClO4 molar ratio of 24. Such negative dependence of intrusion pressure on concentration has never been observed previously. The behaviour of “MFI-type zeosil – NaClO4 solution” systems changes also with salt concentration. For the most concentrated solutions, the first intrusion is only partially reversible, a part of the solution remains trapped into the pores, but this part decreases with solution dilution. A similar phenomenon is observed for *BEA-type zeosil (3D channels with 12 MR pore openings): the intrusion pressure of NaClO4 solutions is always lower than the one of water. By the same manner, it increases slightly with solution dilution.

However, this effect depends on zeosil structure. Contrary to the MFI- and *BEA-type zeosils, the intrusion pressure of NaClO4 solutions in the CHA-type one with narrower pore openings (3D cages, 8 MR) is always higher than the water one and increases strongly with salt concentration. It can be supposed that the negative dependence of intrusion pressure on concentration for MFI- et *BEA-type zeosils is explained by the affinity of perchlorate ions to the frameworks when this factor dominates the one of osmotic phenomena and distortion and dehydration of solvated ions. However, when the solutions are intruded in narrower pores of CHA-type zeosil, the impact of osmotic and dehydration processes becomes predominant and the pressure dependence becomes normal.

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1181 - GREEN KINETIC PROMOTERS FOR SUSTAINABLE ENERGY STORAGE IN ZEOLITIC ICE

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Zeolitic ices are promising materials for safe and compact energy storage, buttheir wide-scale application is hindered by slow formation kinetics [1]. We first revealed the role of acidic zeolites such as Y-H to enhance the kinetics and conversion of methane gas hydrates [2]. To further boost the economics of the process, we showed that a more hydrophobic zeolite (USY-40) has a superior performance over a hydrophilic one (USY-10) to enhance the methane uptake and the kinetics of hydrates formation from seawater at ambient condition. The results showed that gas uptake could reach 40 mmol of gas/mol of water, the highest reported under mild conditions using seawater [3].In this study, we further investigated the effect of another acidic zeolite (H-SSZ-13) and amino acids (l-tryptophan, l-leucine, and l-methionine) as green kinetic promoters in a novel reactor design to accelerate hydrate formation at 6 MPa.

In a non-stirred reactor (NSR), H-SSZ-13 and l-tryptophan showed superior performance over l-leucine and l-methionine. While H-SSZ-13 showed the lowest average t90 (time taken for 90% completion of methane uptake) of 286 mins and the highest volumetric capacity of 115 v/v at 283 K, its kinetic performance, along with other promoters, dropped significantly at 293 K. We also introduced a new fixed bed reactor (FBR) equipped with light metallic packing filaments (MPF) to increase gas diffusion and thermal conductivity. The combined effect of FBR-MFP reactor with zeolite significantly improved the kinetics overcoming NSR drawbacks. At 293.15 K, H-SSZ-13 acidic zeolite promoter showed superior performance reducing the induction time and t90 to 3 and 154 mins, respectively. Furthermore, it exploited 88.6% and 96% of the sII clathrates volumetric storage capacity at 293 K and 283 K, respectively. Finally, we showed that the synthesized hydrates can be stored at atmospheric pressure for 4 months without a significant methane loss. This multiscale approach paves the way for green and economical gas hydrate technology scaling up.

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1318 - 2D COBALT MOF NANOSHEETS FOR SUPERIOR ELECTROCATALYTIC WATER OXIDATION IN NEUTRAL MEDIA

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Water splitting is one of the key processes for many applications related to energy storage and conversion. Water oxidation or oxygen evolution reaction (OER) is still considered the most challenging step in water splitting since it is a more complex transformation than proton reduction. Cobalt-based metal organic frameworks (MOFs) have recently attracted great interest due to their notable electrocatalytic OER activity and the abundance of this metal in the earth.[1]

Herein, a new cobalt metal−organic framework (2D-Co-MOF) based on well-defined layered double cores that are strongly connected by intermolecular bonds has been developed (Figure 1a).[2] In situ electrochemical activation of a 2D-Co-MOF@Nafion composite deposited on a graphite electrode produces a well dispersed and ligated nanostructuration of the composite promoting intimate interactions between both components, and more abundant electrochemical active sites, where metal centers retain its coordinative chemistry thereby without affecting the intrinsic electrocatalytic properties of the active cobalt centers for OER.[3] The so-activated 2D-Co-MOF@Nafion exhibits an outstanding electrocatalytic performance for the OER at neutral pH and a high robustness (Figure 1b). The particular coordination chemistry of the MOF consisting of a regular arrangement of multiple Co(II) redox metal sites connected by appropriate organic ligands can explain the higher catalytic activity of the present MOF.

1182 - LIGHT OLEFINS THROUGH DIMETHYL ETHER CONVERSION OVER MFI TYPE ZEOLITES EFFECT OF SUPERFICIAL PASSIVATION ON CATALYTIC PERFORMANCE AND STABILITY

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Light olefins like ethylene and propylene are important components for the petrochemical industry since they are involved in the plastics production and in the synthesis of various chemicals. Olefins can be obtained through the conversion of dimethyl ether (DME) according to DME-to-olefins (DTO) process. If DME is obtained through the hydrogenation of captured carbon dioxide (and H2 is generated by exploiting renewable energy), the production of light olefins would occur according to a sustainable and green pathway. DTO is usually carried out at a temperature range of 300-450 °C in presence of an acid catalyst; the most investigated materials are SAPO-34. and HZSM-5 zeolites. In this work, MFI-type zeolites with and without superficial passivation by using Silicalite-1 have been investigated.

MFI-type zeolite with Si/Al equal to 25 (MFI-25) was synthesized by preparing a synthesis gel including NaOH, SiO2, Al2O3, H2O and tetrapropyl ammonium bromide (TPABr) acting as structure directing agent (SDA). After the hydrothermal synthesis carried out at 170 °C for five days, the obtained sample was washed with water and calcinated at 550 °C to eliminate the SDA. Acid form of the zeolite was obtained via two ion exchange cycles with NH4Cl (1 M) followed by calcination at 550 °C [1]. The 'passivated' sample (PAS-25) was obtained by depositing a thin double layer of Silicalite-1 on the corresponding MFI particle in its 'as-made' form (i.e., after the hydrothermal synthesis and before the first calcination for SDA removal) according to the "epitaxial growth" technique [2]. The samples were as well washed, dried, and then ion exchanged and calcined at 550 °C twice. The crystalline structure of samples was analyzed by X-ray powder diffraction. Si/Al ratio was measured by atomic absorption spectroscopy. Textural properties were determined by adsorption/desorption isotherms of N2 at 77 K. Fourier transform infrared spectroscopy (FT-IR) was used to evaluate Bronsted and Lewis acid sites concentration. Catalytic tests were carried out by feeding a gas mixture containing 3 mol.-% of DME diluted with nitrogen at 2 bar and at a temperature range of 300-375 °C. A space velocity of about 1 gcat h molC-1 was chosen. The gaseous fraction of the outlet stream was analyzed by means of a gas chromatograph equipped with two columns, a thermal conductivity detector (TCD) and a flame ionization detector (FID). Time-on-stream (TOS) tests up to about 14 hours were carried out to investigate catalyst deactivation.

MFI-25 sample shows faster deactivation than PAS-25 especially at higher temperature. This behavior can be ascribed to a different distribution of acid sites in the passivated sample, because superficial acidity is inhibited by the deposition of Silicalite-1 layer. Light olefins (i.e., ethylene, propylene and butenes) shows a cumulated selectivity in the range 40-60 %, with increasing values at higher temperature (e.g., about 60 % for MFI-25 at 375 °C). More specifically, propylene is the most abundant product. A certain amount of methanol is produced besides hydrocarbons. Methanol selectivity is higher for PAS-25 (having slightly lower acidity), and its content is greater when operating temperature is lower. It is worth noting that as the deactivation proceeds, the methanol selectivity increases progressively. The experimental campaign showed that passivation represents a useful synthesis technique to limit the deactivation of the catalyst over time, improving its stability and keeping high DME conversion rates.

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CATEGORY: DECARBONIZATION AND CO2 MANAGEMENT

1007 - CO2 AS AN OXIDANT DURING DEHYDROGENATION OF PROPANE TO PROPENE OVER ACTIVATED CARBON BASED CATALYSTS

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Propene is an important chemical in the petrochemical industry and is used for the synthesis of polypropylene plastics, propylene oxide, acrylonitrile, cumene, acrylic acid, etc. It is currently produced on the ~100 Mt/year scale by a very energy intensive naphtha steam cracking process. New and more environmentally friendly catalytic processes for propene synthesis are intensely investigated. Activated carbon materials with large surface area and pore volume have an increasing number of applications as catalyst supports and adsorbents. They can be synthesized in a variety of morphologies and their surfaces can be functionalized with different dopants or oxygen containing groups, giving rise to catalytic activity in many reactions, including oxidative dehydrogenation of propane. This contribution is focused on the systematic analysis of propane and CO2 interaction with activated carbon (AC) supported catalysts. CeO2, V2O5 and CeVO4 were synthesized as bulk oxides, or deposited over activated carbon in different loadings. Characterization was performed by XRD, HRTEM, CO2-TPO, C3H8-TPR, DRIFTS and Raman techniques and tested in propane oxidative dehydrogenation reaction using CO2 as a soft oxidant.

By combining characterization and catalytic data, we arrived at the following conclusions: Reduction of CeO2 based catalysts by propane, and their re-oxidation by CO2 are fast under reaction conditions and the propane dehydrogenation reaction proceeds via lattice oxygen participation. Unfortunately, the main reaction pathway over cerium containing catalysts is the total oxidation of propane.

During propane oxidative dehydrogenation (ODH reaction), V2O5 is irreversibly reduced to V2O3, which leads to a progressive shift from propene selectivity to the propane cracking reaction which yields H2, CH4 and C2H4. The participation of CO2 in the reaction is negligible and the reaction pathway is governed by the availability of lattice oxygen in V2O5 and V2O4. The V2O3 phase, formed in-situ during reaction, preferentially catalyses propane cracking.

In the VOx/AC catalysts, a vanadium carbide phase is formed exclusively at vanadium loadings up to 5 wt. %, whereas vanadium carbide and V2O3 phases coexist at larger vanadium loadings. In addition to acting as the support, the activated carbon acts as a reducing agent and is responsible for the transformation of initially present VOx phase to VC. By combining the C3H8-TPR, CO2-TPO, and catalytic results we can postulate that CO2 activation over the VC crystals is assisted by the adsorbed propane. The deactivation of VOx/AC catalysts is accompanied with a stable propene selectivity, which indicates the total number of active sites and not their nature is changed with TOS. Oxidation of the VC phase during the propane-CO2 ODH reaction does not occur. As a result, deactivation is probably related to blocking of the active sites by carbon.

The active site for the propane ODH reaction in the CeVO4/AC catalysts is a thin (1-2 nm) amorphous CeVO4 layer which covers the CeVO4 crystals. During reaction, crystallization of the amorphous CeVO4 layer and surface covering with carbon, which are the causes of catalyst deactivation.

To summarize, the AC support performed several roles, such as enabling high dispersion of nanometer-sized active clusters which influenced their catalytic activity and selectivity. AC also enabled in-situ formation of new, never before tested carbidic phase, which is active and selective for the propane oxidative dehydrogenation reaction.

1080 - TWO AND THREE CO2 MOLECULES BONDED TO ONE CATION EXCHANGED IN FAUJASITE

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In order to design effective CO2 capture materials, it is necessary to ensure high adsorption capacity and suitable binding energy. Here we present a detailed combined FTIR spectroscopic and DFT study of CO2 adsorption on NaY and CaNaY zeolites. Adsorption of CO2 on NaY at ambient temperature and pressures up to 100 mbar leads to formation of Na+···O=C=O adducts characterized by a ν3(12CO2) band at 2354 cm-1 and the respective ν3(13CO2) satellite at 2288 cm-1 [1]. Lowering temperature in presence of CO2 lead to two effects. First, CO2 molecules change their orientation. The process results in a small red shift of the ν3(13CO2) mode. The position of the ν3(13CO2) band was impossible to follow precisely at high coverages due to its extremely high intensity. A second CO2 molecule then attaches to the same Na+ site thus forming geminal species. In this case, 13CO2 molecules become part of Na+(12CO2)(13CO2) adducts and the ν3(13CO2) mode shifts to 2278 cm-1. The results demonstrate the possibility of simultaneous binding of two CO2 molecules to one cationic site in zeolites, which opens new horizons in the design of high-capacity CO2 adsorbents. However, the formation conditions of the geminal species in NaY (low temperature or/and very high equilibrium pressure) are not of practical interest. We therefore decided to change the nature of the exchanged cation. We have chosen Ca2+ because it possesses a similar ionic radius but higher electrophilicity than Na+.

Indeed, it was revealed that that one Ca2+ site in CaNaY can attach up to three CO2 molecules. At ambient temperature, geminal adsorption complexes are produced at < 1 mbar CO2, and tri-ligand species begin to form at ca. 60 mbar. A stepwise conversion between mono-, di- and tri-ligand species was also found upon lowering the temperature. The ν3(13CO2) mode appears at 2298, 2293 and 2289 cm-1 for the complexes with one, two and three CO2 ligands, respectively. The 12CO2 molecules in the polyligand complexes interact vibrationally. Thus, while the Ca2+(12CO2) species exhibit only one ν3 band at 2364 cm 1, the geminal Ca2+(12CO2)2 species are characterized by in-phase and out-of-phase ν3 modes at 2367 and 2354 cm-1, respectively. Despite the very high intensity of the ν3(12CO2) mode, we identified one band of the Ca2+(CO2)2 species at 2372 cm-1. These observations correlate well with the fact that up to three CO molecules can be adsorbed on one Ca2+ site in CaNaY [2].

We also complemented the experimental observations with computational modeling using periodic density functional calculations. The optimized structures include one, two- and three ligand species, and the calculated frequencies match the experimental ones very well. Finally, we emphasize that CaY zeolites possess a high CO2 adsorption capacity at ambient temperature. Each Ca2+ site can attach two CO2 molecules at relatively low partial pressure and has the reserve potential to attach an additional CO2 molecule when the equilibrium pressure is higher. We believe that the results will contribute to the development of CaY-based adsorbents for CO2 with high adsorption capacity.

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1130 - POSSIBLE CO2 CAPTURE AT A NANOCONFINED LIBH4 IN THE PORES OF ZIF 8

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The known zeolitic imidazolate framework ZIF-8 was impregnated with a LiBH4 solution in diethyl ether, which was subsequently evaporated, leaving LiBH4 particles in the large (1.16 nm diameter) pores of ZIF-8.

Proving that LiBH4 is truly nanoconfined in the pores of ZIF-8 and not just deposited outside between the ZIF-8 crystallites was challenging. XRD showed that the crystallinity of ZIF-8 is preserved, but no measurable change of the unit cell parameters or intensity ratios could be detected due to the weak scattering power of LiBH4. XPS indicated the presence of boron in the sample and its uniform distribution in the depth profile. Most convincing were the IR spectra of ZIF-8/LiBH4 samples exposed to air for different lengths of time. The presence of broad signals characteristic of BH4- species were evident in the IR spectra between 4000 and 2195 cm-1 and they gradually disappeared when the material was exposed to air. From experience, it is known that pure LiBH4 completely decomposes in air within a few seconds, while the signals in the IR spectra show that the nanoconfined ZIF-8/LiBH4 survives for several minutes.

Further indication for nanoconfinement of LiBH4 in ZIF-8 was obtained by TG/MS/DSC, which showed that hydrogen is released from the samples in an endothermic process at about 120 oC. This is much lower than for LiBH4 in bulk (above 300 oC). Quantum chemical calculations indicated that the formation of LiBH4 clusters in the pores of ZIF-8 is possible and that the interactions between Li+ and BH4- strongly predominate over their interactions with the framework. The stability of the clusters increases with the number of entrapped ions, qualitatively suggesting that nanoconfined LiBH4 clusters are less stable than the bulk material, consistent with their lower dehydrogenation temperature.

In addition, the sorption isotherms for nitrogen and hydrogen show that the adsorption surface area in ZIF-8/LiBH4 is lower than in pure activated ZIF-8, suggesting that LiBH4 occupies part of the available pores.

The sorption isotherm of CO2 on ZIF-8/LiBH4 differs significantly from that of pure activated ZIF-8. The sorption capacity of 1.4 mmol/g(ZIF-8/LiBH4) at 1 bar and room temperature is much higher than 0.8 mmol/g(ZIF-8). The sorption isotherm of CO2 on ZIF-8/LiBH4 exhibits hysteresis (0.9 mmol/g remains adsorbed at 0.02 bar) and the adsorption enthalpy of -121 kJ/mol indicates a strong (chemical) interaction of CO2 with ZIF-8/LiBH4, while the interaction of CO2 with pure activated ZIF-8 is a typical physisorption (-17 kJ/mol).

One possible reaction would be the formation of formatohydridoborates, known from the literature [1], where BH4- anion reacts with up to three molecules of CO2, in this case forming triformatohydridoborate [BH(OCHO)3]-.

The presentation will explain the experimental and theoretical evidence for the above. Since the studies of the ZIF-8/LiBH4/CO2 system are still in progress, some new results may be added.

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1155 - 6LI SOLID STATE NMR STUDIES ON LI+ CHA TYPE ZEOLITE FOR N2 AND O2 ADSORPTION

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Oxygen generation from air through pressure-swing adsorption (PSA) is essential to achieve highly efficient O2 combustion in thermal power plants, thus reducing CO2 emissions. The PSA process uses Li-LSX, which is a very low-silica FAU-type zeolite (Si/Al = 1.0) with the maximum content of Li+ (Li/Al = 1.0).1) The preferential adsorption of N2 on Li+ in zeolites is attributed to the interaction between the quadrupole moment of the N2 molecule and electric field gradient on the micropore surface of the zeolites.2) Among the Li+ species in Li-LSX, those located at SIII sites in the FAU framework, which consists of double-6-ring (d6r) aluminosilicate components, enable effective N2 adsorption.1, 3) Furthermore, CHA-type zeolites, which are composed of the ABC stacking sequences of d6r components, reportedly contain Li+ species, which are effective for N2 adsorption.4) In this study, low-silica CHA-type zeolites (Si/Al = 2.4) with high Li+ content (Li/Al = 0.3−1.0) were prepared. Thereafter, N2 and O2 adsorption isotherms for the Li-CHA samples were obtained at 25 °C to investigate the N2/O2 adsorption separation ability of the zeolites. Moreover, 6Li solid-state MAS NMR spectroscopy was conducted to identify the Li species in Li-CHA that are effective for N2 adsorption.

K-CHA (Si/Al = 2.4) was obtained by the hydrothermal treatment of the FAU-type zeolite (Si/Al = 2.85) in an aqueous KOH solution. First, the as-prepared K-CHA was totally ion-exchanged into Na-CHA in an aqueous NaCl solution. Then, (Li, Na)-CHA samples with different ion-exchange ratios were prepared by a similar treatment of Na-CHA in an aqueous LiCl solution. The Li/Al ratio is denoted in square brackets in the sample name, e.g., CHA[1.0]. Commercially available Li-LSX (Si/Al = 1.0, Li/Al = 1.0) was used as a reference. The N2 and O2 adsorption isotherms (25 °C) were measured after pretreatment at 400 °C for more than 12 h in vacuo (< 1 Pa). 6Li MAS NMR spectroscopy (9.4 T) was performed on the samples exposed to an O2 atmosphere at room temperature after pretreatment at 200 °C in vacuo (< 1 Pa). For comparison, the samples exposed to air were subjected to NMR analysis.

The N2 adsorption capacity of CHA[1.0] was 1.50 mmol-N2/g-zeolite at 100 kPa, higher than that of LSX[1.0] (1.04 mmol-N2/g-zeolite), and the N2/O2 adsorption ratio of CHA[1.0] was 4.0. Notably, the ratio of the amount of N2 adsorbed to the amount of Li in the zeolite was 0.50 for CHA[1.0], which is much higher than that (0.17) for LSX[1.0]. This suggests that the CHA-type zeolites contain more Li+ species that are effective for N2 adsorption than LSX.

In the 6Li MAS NMR spectra of Li-CHA[1.0], a change in the chemical shift of Li occurs due to the paramagnetism of O2. CHA[1.0] exposed to air shows a peak only at −0.4 ppm, while that exposed to O2 shows a broad peak at 1.0 ppm in addition to a peak at 0 ppm. The peak at 1.0 ppm is attributed to the presence of Li+ species influenced by the paramagnetism of O2.5) This implies that the Li species can adsorb N2 as strongly as O2. Thus, we confirm that the Li species effective for N2 adsorption could be identified.

1165 - CARBON CAPTURE IN FULLY HYDRATED MORDENITE

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Incorporation of zeolites in cement-based materials are currently being explored as a method of increasing the carbon uptake of cement-based built infrastructure. Cement is one of the most widely used man-made materials[1] and cement binder has an intrinsically high carbon footprint from the calcination reaction and high temperature processing conditions.[2] One approach to decarbonize concrete is to increase carbon adsorption through the incorporation of a porous supplemental cementitious material (SCM) to capture CO2 inside the pore space and increase the carbonation depth. Zeolites are a candidate due to their carbon capture capabilities and stability in high pH conditions.[3] Within a cement matrix, zeolites would be fully hydrated from water used during concrete synthesis. There is only a limited understanding of how CO2 interacts with bulk aqueous conditions inside zeolites. Therefore, density functional theory simulations (DFT) were used to evaluate the stability of CO2 in fully hydrated mordenite structures. Mordenite zeolite was selected as a prototypical aluminosilicate zeolite for evaluation of confined structure and stability of CO2-water mixtures. Three different mordenite systems were evaluated, including pure silica mordenite (Si-MOR), protonated mordenite (H-MOR), and sodium mordenite (Na-MOR) with a Si/Al ratio of 5:1 which have been previously evaluated for their use in in-situ formation of Ag0 clusters.[4, 5] Through analysis of the binding energies and structures of CO2-water mixtures in these systems, the reactivity of H2O-CO2 mixtures were evaluated along with the prediction of in-situ carbonate formation. Overall, high hydration levels were identified inside the MOR structures, with some CO2 stability at low concentrations. The existence of CO2 clusters inside the main channel of the pore was evaluated, along with preferred CO2 binding sites and hydration shells. Overall, the fundamental understanding generated from the molecular scale evaluation of zeolites with a mixture of gas molecules can be used to design zeolite-cement compositions with varying carbonation rates and capacities.

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1183 - TUNING OF CO2 CAPTURE AND CONVERSION PERFORMANCES BY CATION EXCHANGE IN METAL ORGANIC FRAMEWORKS

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Metal-organic frameworks (MOFs) are excelled for their high modularity of chemical properties which can be achieved via rational design or by using various post-synthesis modification processes. Cation-exhange which is already well established among zeolitic materials, is rapidly gaining interest for MOF structures as well since it can enable fine tuning of adsorption, separation, catalytic or optical properties of MOFs.

In this contribution the investigation of cation-exchange ability and impact on CO2 capture and conversion is presented on porous Zn3(BDC)4(DMA)2 material (BDC = 1,4- benezendicarboxylic acid; DMA = dimethylamine) with DMA+ species balancing the anionic charge of the framework located on protonated carboxylate oxygen atom of the tereohthalate ligand. Dimethylamine cations are located within the Zn-terephthalate framework micropores with dimensions of 0.8 x 0.55 nm and were efficiently exchanged with Li+ , Na+ , K+ and Mg2+ cations. The optimal exchange rates which were determined by ICP-OAS and EDAX elemental analysis was approximately 30 % achieved for all metal cations. The environment and location of exchanged cations within the MOF frameworks, investigated by single-crystal XRD and solid-state NMR techniques, was proved to replace the approximate crystallographic positions of the pristine DMA+ cations. All exchanged materials exhibit notable improvement of CO2 capture parameters such as sorption equilibrium capacity, isosteric heat of adsorption and CO2/N2 selectivity in respect to the parent Zn-terephthalate in the order Mg2+ > Li+ > Na+ > K+. The trend is related to the cationic radii of the exchanged metals. Series of exchanged materials show catalytic activity for conversion of propylene oxide into propylene carbonate in the presence of CO2 at mild conditions (10 bars, 100 °C, 4 hours). The formation of frustrated Lewis acid-base pairs on the form of metal cations and uncoordinated carboxylate oxygen atom respectively, enable notable catalytic activity without using co-catalyst. The catalytic efficiencies follow different trend as observed for CO2 capture performances (Mg2+ > Li+ > Na+ > K+) indicating that Lewis acidity properties of the exchanged-cations play most important role for the CO2 conversion capabilities. Namely, the highest catalytic activity with propylenecarbonate conversion of 30% and selectivity more than 90% is achieved for magnesium cation exchanged MOF possessing highest Lewis acidity among the investigated cations. The latter material was investigated for catalytic durability where the catalyst was regenerated and reused for 5 catalytic cycles. Structure integrity of material is completely preserved after catalysis cycling, however its activity gradually decreases during the cycles due to the partial dissolution of catalyst in propylene oxide.

1209 - FROM POWDER TO 3D SHAPED LTA ZEOLITE FOR CARBON DIOXIDE CAPTURE

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The Carbon Dioxide (CO2) amount in the atmosphere has significantly increased during the last decades, due to the human activities that have irreversibly altered the atmospheric CO2 concentration. Due to the huge amount of CO2 emissions, this molecule remains the major responsible for the greenhouse effect, even if its global warming potential is lower than the one estimated for other GHGs greenhouse gasses. Among the different Carbon Capture and Storage (CCS) technologies to counter CO2 emissions caused by anthropogenic activities, solid adsorbents have gained particular interest thanks to several advantages, as low energy costs, mild regeneration conditions and low volatility of the captured CO2. A class of possible adsorbents for the CO2 capture are zeolites, thanks to their textural, structural and chemical properties, as far as for their high cation exchange potential and polarity properties [1]. However, to increment their industrial applicability, they should meet important requirements as high CO2 sorption capacity, weak regeneration conditions, availability into already shaped form and low costs [2]. Among the synthetic zeolites, LTA (Lynde-Type A), generally applied as an industrial desiccant, seems to meet some of the above reported requirements. This work focuses on the study of a low-cost LTA zeolite and on its applicability as potential CO2 adsorbent. The CO2 adsorption capacity of powder NaLTA as such and after ion-exchange was evaluated in the medium-low temperature range. Subsequently, to facilitate its industrial applicability, the same materials in beads form were investigated in both static and dynamic conditions. Lastly, to further improve the adaptability to industrial conditions, a 3D printed NaLTA zeolite was synthesized and studied. All materials were characterized by applying an advanced multi-technique characterization approach. Their structural and textural properties were evaluated to investigate the accessibility of the ions present inside the microporous structure and the strength of their interaction with the adsorptive by combining gas sorption analysis and in situ infrared spectroscopy. The CO2 adsorption tests were carried out performing pure CO2 adsorption/desorption isotherms and dynamic breakthrough measurements in a wide range of temperature (298-423 K). The 3D printed LTA was also studied in different geometries to evaluate the effect on the dynamic CO2 adsorption measurements. Interestingly, the 3D printed material exhibited at 298 K a CO2 adsorption capacity comparable to the commercial LTA powder.

The materials were also tested with a wet CO2 stream, to assess the adsorption properties in the presence of moisture.

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1220 - NOVEL ZTC MATERIALS FOR THE ELECTROCATALYTIC UPGRADING OF FURFURAL TO HIGH ADDED VALUE PRODUCTS

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The continuous and growing demand for energy production accompanied by the depletion of fossil fuels has led the scientific community to search for alternative renewable sources for the production not only of energy but also of high added value chemical products. A possible transition towards a sustainable chemical industry could be based on the use of "green" raw materials of natural origin, such as biomass. Alongside the traditional thermocatalytic route, in the last years there is an increasing interest towards the electrocatalytic route due to the possibility to carry on the reaction under milder conditions, and especially to couple in tandem with a reduction reaction on the electrocatalytic reactor to obtain process intensification [1]. For these new catalytic processes zeolite templated carbons (ZTC) represent a valuable option. Take advantage of the shape-selectivity characteristics of zeolites it’s possible to develop novel 3D-type electrodes, with high conductivity, accessibility and high surface area in order to eventually host metal nanoparticles, to be used in the electrocatalytic oxidation of furfural to high added value products [2]. ZTCs were synthesized through Chemical Vapour Depositions using ethylene as a carbon source at high temperature, starting by homemade zeolites and gold nanoparticles (AuNPs) were deposited on their surface by sol immobilization. All materials were in depth characterized using different techniques as N2 adsorption, X ray diffractions (XRD), Raman spectroscopy and SEM/EDS analysis. The characterization results evidenced a good replication degree of zeolite frameworks presenting a prevalent microporous structure with extensive surface area (up to 3000 m2/g). These textural features are preserved also after AuNPs deposition. SEM/EDS analysis shows a good dispersion of AuNPs on ZTC supports.

These materials were used for the fabrication of the working electrodes by depositing on a gas diffusion layer (GDL) by airbrushing and their electrocatalytic behaviour was studied in the electrocatalytic oxidation of furfural using a commercial flow cell in a three electrode configuration. The electrocatalytic tests were performed using different electrolytes (KOH, H2SO4 and HClO4) in order to study the effect of the nature of the electrolyte in the reaction pathways. The results confirmed that the use of a basic electrolytes leads to the formation of furoic (FA) and maleic acid (MA) instead the use of acidic media favours the selective formation of 5-hydroxy-furan-2(5H)-one (5-HFN) and MA. Moreover, using the metal-free ZTC materials in HClO4 was possible to obtain a faradaic efficiency towards 5-HFN about 90%, instead the deposition of gold nanoparticles allows to achieve an almost total selectivity (98%). The results were compared with those obtained by thermocatalytic oxidation of furfural with O2 using methanol as solvent and in the absence of added bases.

These results highlight the potential use of ZTC as electrocatalysts for electrochemical applications in biomass transformation for chemical production.

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1233 - MACROSCOPIC ZEOLITIC BEADS WITH HIERARCHICAL POROSITY AS VERSATILE HETEROGENEOUS CATALYSTS AND CO2 ADSORBENTS

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For important industrial applications in heterogeneous catalysis and as adsorbents for separating CO2 from CH4 (in biogas) or from N2 (in flue gases), zeolites generally need to be shaped in the form of macroscopic pellets to minimise issues caused by pressure drop. This is typically realised using a binder to shape the zeolite powders into the desired pellet format. However, using a binder also has downsides as it leads to a decrease in specific surface area and possible partial blockage of the zeolitic micropores. An attractive alternative consists in preparing zeolite in the form of macroscopic beads (0.3-1.0 mm, Fig. 1) using ion-exchange resin bead as hard template. Using carefully tailored hydrothermal methods, it is possible to achieve the growth of zeolite crystallites with the resin bead template. Upon calcination, the template is removed leaving behind zeolitic beads in which the microporous zeolitic domains are accessible through a hierarchical network of meso- and macropores, thus enabling efficient diffusion of molecules.
Here, we will present the results achieved by our group in recent years in the synthesis of several types of zeolitic beads with hierarchical porosity (zeolite Y, Beta, ZSM-5, LTA and SAPO-34 frameworks) and their application as heterogeneous catalysts and as adsorbents for the selective adsorption of CO2. Zeolitic beads in H-form were investigated as heterogeneous catalysts in the Friedel-Crafts acylation of anisole with acetic anhydride to produce paramethoxyacetophenone (Fig. 2), with zeolite Beta beads displaying the best catalytic performance (95% conversion of acetic anhydride and 76% yield of para-methoxyacetophenone after 6 h at 90 °C in a batch reactor and better performance than conventional pellets in a fixed-bed reactor). [1] Bimetallic zeolite Beta beads with a combination of Brønsted and Lewis acid sites obtained by post-synthetic dealumination followed by grafting with Sn, Zr or Hf were studied as heterogeneous catalysts in the conversion of bio-based dihydroxyacetone to methyl lactate. The Sn-containing zeolite Beta beads displayed the best catalytic activity, and achieved 90 % yield of the lactate with 99% selectivity after 6 h of reaction at 90 °C. [2] Zeolite LTA and SAPO-34 beads, having smaller pore apertures, are suitable for selective CO2 adsorption (Fig. 3). Promising results were obtained by partially ion-exchanging zeolite Na-LTA beads with K+, achieving very high CO2/CH4 selectivity (1540) while preserving high

CO2 adsorption capacity (1.9 mmol/g 1 at 0.4 bar CO2, i.e. the partial pressure of CO2 in biogas). [3]. Finally, we demonstrated the possibility of preparing zeolite beads with a core-shell structures consisting of a ZSM-5 core suitable for CO2 adsorption and silicalite-1 hydrophobic shell that allowed minimising the undesired adsorption of H2O.

1258 - ZEOLITES AS THE FLEXIBLE PLATFORM FOR DEVELOPING METAL SUPPORTED CATALYSTS FOR CO2 VALORISATION REACTIONS

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Zeolites plays a key role as catalysts and/or catalyst carriers in CO2 valorisation which requires catalysis to enable the process efficiency. The stable crystalline structure and the tuneable porous framework provide excellent flexibility for developing various metal incorporation methods which helps the understanding of relevant catalytic systems and improves the activity. Catalytic CO2 methanation and dry reforming of methane with CO2 are two common systems investigated to achieve the CO2 conversions to value added chemical and fuels, yet the two systems experience many challenges such as deactivation due to metal sintering and coke formation. In this presentation, our studies in rational catalyst design based on zeolites to improve catalytic efficiency of the two systems will be presented. The design strategies employing the flexibility of zeolites will be discussed and shared. For example, (i) exploration of effect of metal accessibility on plasma-assisted CO2 methanation was achieve by tuning the porous structure of siliceous MFI zeolites and (ii) investigation of encapsulation strategy for improving metal segregation and dispersion to address the deactivation issues experienced by dry reforming of methane with CO2. The presentation will also discuss the prospects of zeolite research towards catalyst development for other catalytic applications in sustainable chemistry for achieving the Net Zero goal.

1262 - CATALYTIC DECOMPOSITION OF METHANE FOR PRODUCING HYDROGEN GAS AND CARBON NANOTUBES

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Hydrogen production methods from fossil and renewable biomass resources include steam reforming and pyrolysis. Contrary to steam methane reforming where beside hydrogen waste carbon dioxide is produced, in the catalytic decomposition of methane (CDM) hydrogen with solid carbon is formed. CDM or methane pyrolysis is a promising technology, because during the process carbon-oxides free ’turquoise’ hydrogen is formed, which is ideal for fuel cell applications, and the carbon by-product can be tailored into advanced morphology (nanotubes, nanofibers, etc.). CDM can be carried out over conventional solid catalysts or in molten metals/salts. One drawback of the technology is that it requires high operating temperatures, therefore often nickel containing solid catalysts working at the lowest temperature range (500-800°C) are used [1].

Ni-containing porous materials can also be applied in this process, and some examples from the literature will be overviewed. Effective methane decomposition with high carbon nanofiber yields was found over Ni/Y zeolite catalysts [2]. Higher dispersion and surface area of active Ni metallic particles resulted formation of higher H2 and graphitic nanocarbon production in CH4 decomposition on composite Ni/HZSM-5/MCM-41 catalysts [3].

Modification of nickel by molybdenum can improve methane pyrolysis producing uniform, narrow nanotubes [4], but the bimetallic cooperation is not clarified yet. Our aim is to develop long-life CDM catalysts combining Ni with Mo/MgO, which produce valuable nanostructured carbon products. We prepared Ni/MgO, Mo/MgO and NiMo/MgO catalysts with 7 wt% Ni and 4wt% or 13wt% Mo content by adsorption/precipitation followed by calcination at 550°C and reduction at 800°C. The bimetallic catalyst samples were differentiated by the Mo/Ni atomic ratio (MoNi0.4 and MoNi1.2). Only the NiMo samples were reduced completely to metallic Ni and Mo species. The average particle size for all samples varied between 5-8 nm. XRD of MoNi1.2 sample indicated MgO reflections only suggesting the highest metal dispersion. The catalytic properties were determined in a pyrolysis test reactor with 50% CH4/Ar flow at 800°C and GC gas product analysis. Only hydrogen gas-phase product was detected and the measure of catalytic activity was the decomposition rate of methane. The amount of carbon produced after pyrolysis was determined by mass measurement, or was calculated from the amount of decomposed methane. The carbon formed on Ni/MgO during pyrolysis was the most graphitic (intensity ratio of Raman D and G bands, IG/ID=7.7), while on Mo/MgO it was the most defective (IG/ID =0.4), in both cases covering the Ni- or Mo-carbide particles with a few layers, often partial shells, resulting in rapid deactivation of both samples. A synergetic effect over the bimetallic catalysts was found, the best MoNi1.2 catalyst yielded 300% carbon, partially defective (IG/ID=3), multi-walled carbon nanotubes with a maximum diameter of 10 nm. We explain the exceptional CDM activity of the bimetallic MoNi1.2 sample by the high and stable dispersion of bimetallic NiMo particles with a special 1:1 composition. We plan to extend our studies over NiMo/zeolite catalysts.

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1279 - TRULY COMBINING THE ADVANTAGES OF ZEOLITE AND POLYMERIC MEMBRANES SSZ 39 POLYIMIDE MEMBRANES WITH UNRIVALLED PERFORMANCE FOR CO2 REMOVAL

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The separation of CH4 and CO2 (and even N2) is often regarded as a crucial part of the processing of gas streams such as biogas or natural gas, to increase the caloric value and reduce corrosion caused by acidic CO2. Now, this separation is achieved through multiple techniques such as cryogenic distillation or pressure swing adsorption. Yet these have their drawbacks, including high energy consumption or large and costly initial capital investment.[1] One alternative is to perform the separation with membranes. Due to their fixed pore size in the right size range of these molecules (Kinetic Diameter CO2: 3.3 Å) [2], small pore zeolites, such as AEI (3.84 × 3.64 Å) [3] are seen as promising materials to perform this separation, however, their incorporation into a membrane remains challenging, as pure zeolite membranes are difficult to synthesize and are often too brittle to utilize in the industrial conditions. Mixed matrix membranes (MMMs), a type of membrane in which fillers are mixed in with a polymer, combine the benefits of both materials, with both flexibilities, high selectivity and permeability. These materials thus have more desireable properties for industrial applications. However, due to suboptimal zeolite-polymer compatibility, MMMs with high zeolite loadings are difficult to achieve.

Herein, we report a feasible thermal annealing procedure which is capable of promoting a good interface between the Na-SSZ-39 zeolite and the glassy polymer (Matrimid® 5218).[4] This resulted in a membrane with an ultra-high zeolite loading up to 50 wt.%, a stunning CO2/CH4 mixed gas selectivity of approximately 423, which is a 10-fold increase compared to the unfilled membrane, and an unparalleled CO2 permeability of ~8300 Barrer. This membrane thus outperforms all existing polymer-based membranes and even many zeolite-only membranes. The unprecedented membrane performance was ascribed to the properties of the zeolite filler, as simulations and gas uptake isotherms confirmed. Methane was shown to be kinetically hindered from diffusing through the eight-membered rings of the zeolite at ambient temperatures. Additionally, due to the presence of Na+-cations, the zeolite displayed a preferential uptake of CO2 over CH4 (CO2-philicity). Moreover, the CO2/N2 separation performance also exceeded the present state-of-the-art. In addition, the effect of the morphology of the zeolite, varied from synthesis, showed the benefits of high aspect ratio platelet-shaped fillers over lower aspect ratio cuboid fillers. By increasing the zeolite loading, platelet-shaped SSZ-39 zeolite crystals were capable of forming a nearly-continuous gas permeation pathway across the membrane at lower loadings than their cuboid counterparts.

In conclusion, next to record breaking CO2 separations (Tan et al., Science, 2022),[4], the techniques described here are suspected to be able to be generalized to different polyimide-zeolite membranes, thus opening the door for developing flexible high-performance zeolite-filled membranes for various applications.

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Science, 2022, 378 (6625) 1189-1194

1280 - RU SUPPORTED ON ZEOLITES FOR CO2 METHANATION INFLUENCE OF PREPARATION CONDITIONS

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Over the past decades, the intensive utilization of non-renewable energy resources, such as fossil fuels, led to an increase of the CO_2 emissions in the atmosphere, being responsible for human-induced climate change. Therefore, different strategies have been studied in order to reduce and control CO_2 emissions, namely CO_2 capture and storage or its conversion into useful chemical compounds and fuels. In this scenario, conversion of captured carbon dioxide into fuels, using green hydrogen produced via water electrolysis with renewable energy refers to Power to Gas (PtG) concept. This process allows not only to reduce the CO_2 concentration on the atmosphere, but also to store the excess of renewable energies, being an effective solution to the intrinsic intermittency of renewable and green resources. Hence, it demonstrates great potential regarding environmental sustainability and economic development. Among the possible CO_2 utilization routes, its conversion to CH_4, as a substitute to natural gas, via Sabatier reaction has gain interest. Synthetic natural gas (SNG), which demand has steadily increase, is considered a clean energy and an interesting energy vector, since it can be directly injected into already existed natural gas grid [1].

Taking into account that CO_2 is a very stable molecule and the exothermicity of this reaction, innovative and stable catalysts are needed to achieve adequate CO_2 conversion and selectivity towards CH_4. Transition, mainly Ni, and noble metals supported on different metal oxides (SiO_2, Al_2O_3, TiO_2, ZrO_2, CeO_2) have been investigated for this reaction [2]. However, Ni-based catalysts still present some challenges as instability, sintering and deactivation in presence of oxygen in real effluents. In this way, noble metals represent an alternative with higher activity, due to the strong ability to activate CO_2 and dissociate H_2, providing a decrease in the reaction temperature. Although their higher cost, noble metals are more resistant than Ni in oxidizing atmospheres, it shows a higher sulphur tolerance, and carbon deposition and sintering are both inhibited.

In this work, the influence of the preparation conditions on zeolite-supported noble metal catalysts properties and performances were investigated. Catalysts were characterized with several techniques (XRD, TGA, H_2-TPR, N_2 adsorption) and tested between for the CO_2 methanation reaction.

Results showed that the preparation parameters affect mainly noble metals' particle sizes and dispersion on the zeolite surface. For instance, using an appropriate precursor salt was found to induce a considerably higher catalytic activity related to a boost in the metallic dispersion. Furthermore, tuning the calcination conditions was also found as a promising pathway towards the synthesis of highly active noble metal-based catalysts. Once again, optimized conditions provided smaller noble metal particles with an improved dispersion, which proved to be a key parameter in achieving higher CH_4 yield.

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1292 - DIRECT AIR CAPTURE OF CO2 INTO MODIFIED ZEOLITIC FRAMEWORKS FOR THE PRODUCTION OF PLATFORM CHEMICALS AND GREEN FUELS

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The dire climate changes and related socio-economic changes associated with the increase of atmospheric carbon dioxide concentrations have imposed unprecedented challenge for industry and academia. According to Paris agreement these effects are only avoidable in the foreseeable future if global warming can be strictly kept well below 2°C [1]. This goal is only achievable by the wide-scale sequestration and recycling of carbon dioxide (at least 10 Gt CO2 per year until 2050) [2]. When coupling direct air capture of CO2 (DAC) together with the green hydrogen technology, CO2 can be considered as a future building block for making a wide range of platform chemicals (e.g., methanol, or syngas) and green fuels and therefore would facilitate the transition from fossil- economy to cyclic economy based on encircling CO2 in a closed loop (i.e., circular economy) [3].

The first step for achieving this target is the development of efficient DAC technology for concentrating CO2 from air or at the outlet of industry outlet furnaces. This relies in the first place on the architecture of adsorbent materials able to selectively concentrate the limited CO2 concentrations (400 ppm) from air in the presence of humidity and other interfering atmospheric constituents. In this collaborative work we address the development of new materials and processes for the capture of CO2 from air (direct-air -capture - DAC) and its recycling. Herein, the main challenges for this technology can be summarized as follows: i) the control of the competing adsorption of water with CO2 on active adsorption materials, and ii) the energy input need to adsorb CO2 (normally cryogenic adsorption is needed) or in its recovery by thermal desorption which is done at relatively high temperatures. The updated status of these two steps makes the DAC process cost-inefficient. Based on these criteria we define an efficient adsorbent material to adsorb CO2 at relatively lower temperatures (close to ambient temperatures) in the presence of humidity, and at the same time to enable the desorption of CO2 at moderate temperatures, ideally < 100°C to avoid an energy intensive process.

In our recent studies we tried to systematically modulate the adsorption properties of zeolite 13X adsorbent by hydrophilization using different organic and polymeric substrates. The controlled loading of the zeolite with the selected organic substrate (or polymer) and its thermal treatment can be used to fine-tune and steer the adsorption characteristics of these materials. The coupling of DAC technology with renewable energy concepts together with our recent results from the characterization of the new adsorbent materials under isothermal and dynamic adsorption conditions are topics of the present contribution.

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1341 - INTENSIFICATION OF ONE POT CO2 HYDROGENATION TO DME OVER 3D PRINTED ZEBRA CATALYTIC BEDS

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The process intensification of dimethyl ether (DME) synthesis represents a promising approach to overcome the thermodynamic limitations of the conventional manufacturing processes. In the direct synthesis of DME from CO2 and H2 mixtures, typically carried out between 30-50 bar and 220-260 °C [1-2], the conversion never exceeds 25% and therefore it is necessary not only to identify catalytic systems more active and selective than those already reported to the state of the art, but also the adoption of alternative and more efficient technological solutions compared to conventional ones. The main idea behind this work was to combine a hybrid catalytic system capable of activating CO2 at low temperatures with a solid sorbent within the same reactor for the capture of the water vapor formed during the process, with the advantage of a process integration able to determine an enhancement of the DME yield.

The preparation of the hybrid systems was carried out using a proprietary Cartesian robot for the micro-extrusion on a 3D scale of multifunctional materials, starting from a premixed catalytic paste of copper and other transition metal oxides (Zn, Al, Zr, …) bound with a zeolite matrix. As regards the hydrophilic material, a LTA-type sorbent was used, with an effective capacity in water absorption and ease regeneration without the need for energy-expensive heat treatments. These two parent systems were then combined in a "zebra"-layered catalytic bed, consisting of the regular alternation of synthesis catalyst and absorbent system. The activity-selectivity pattern over the zebra configuration was assessed in a fixed bed reactor between 30 and 50 bar, in a temperature range of 220-260 °C with a feed mixture of H2/CO2/N2 (9/3/1 mol/mol).

The results of the catalytic testing indicate that hybrid catalysts work better than a mixture of pellets in terms of CO2 conversion and DME yield due to proximity of active sites of the parent functionalities. Indeed, compared to the classic synthetic methods, the robocasting procedure really demonstrated the possibility of improving the interaction between catalytic sites of various kinds at a punctual level, while ensuring extraordinary reproducibility and exceptional control of the structural and morphological architecture. With respect to a conventional powdered mono-bed containing the admixed parent functionalities, in the 3D zebra-bed configuration the number and the thickness of catalytic layers were shown to determine a significant increase in CO2 conversion under the adopted experimental conditions (see Fig. 1), without altering the product selectivity.

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CATEGORY: ON THE WAY TO UTILIZATION

1038 - ONE POT SYNTHESIS OF MENTHOL FROM CITRAL OVER NICKEL CONTAINING EXTRUDATES CONTAINING ZEOLITES AND CLAY BINDERS

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One-pot synthesis of menthols from citral (Scheme 1) has been extensively studied in the presence of noble (Pt, Pd, Ir) and non-noble (Ni, Co, Cu) metals in batch reactors illustrating that Ni along with Pd are the most efficient for hydrogenation of citral and intermediate isopulegols to menthols.

Scheme 1. A simplified reaction scheme for citral transformations to menthols with side reactions. Continuous operation compared to a batch mode facilitates economically feasible production, if the catalyst is enough selective and stable. Such operation mode requires the use of shaped catalysts which scale-up is typically not straightforward, also considering that the initial catalyst screening is performed in the kinetic regime, while continuous operation involves mass transfer limitations influencing not only activity but also selectivity.

We have studied one-pot synthesis of menthol using Ni supported on H-Beta-38 with sepiolite, attapulgite and bentonite as binders [1-3]. Different preparation methods for extrudates were used to tune the metal location, which was loaded either on a clay binder, zeolite or both. When Ni was deposited exclusively on the clay binder, the results were less promising compared to nickel deposition on either beta zeolite or on their mixture. Furthermore, the catalyst characterization revealed large changes in textural and acidic properties among these extrudates.

A proper balance of the acid sites of different strength as well as the metal content was beneficial for transformations of citral elevating selectivity to menthol under optimized process parameters. While the catalysts underwent deactivation, a steady-state activity could be reliably reached after an initial period of deactivation indicating that the scale-up of such catalysts could be feasible.

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1054 - CATALYTIC FAST PYROLYSIS ON ZEOLITES ACTIVITY AND STABILITY OF DIFFERENT STRUCTURES AND ACIDIC CATALYSTS FOR ANISOLE TRANSFORMATION

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The landscape for both petrochemical, oil, and gas industries is evolving to develop more “high-value chemicals” (HVCs) as aromatics (notably BTX : Benzene, Toluene, Xylenes). The majority of BTX aromatics originate from catalytic reforming and FCC units located in refineries. The catalytic fast pyrolysis (CFP) of biomass represents an interesting route for producing green aromatics and olefins by mimicking the fluid catalytic cracking of crude oil[1,2]. Despite the growing interest in biomass CFP, this process is still in its infancy compared with other thermochemical technologies (gasification or combustion). It requires the development of more stable catalysts (which are, at the moment, very susceptible to coke deposition and deactivation), with increased BTX selectivity. Thus, mastering catalyst stability has become as essential as regulating selectivity and activity, as is understanding the mechanisms leading to deactivation and changes in selectivity. Because biomass is such a complex and diverse feedstock, anisole was chosen to be a model molecule for all the methoxy group-containing primary pyrolysis products of lignocellulosic biomass.

The transformation of anisole was carried out over HFAU (Si/Al = 15), HBEA (12,5) and HZSM-5 (9<Si/Al<201, emphasis on Si/Al = 43) catalysts (at almost iso-acidity) at 400°C, under atmospheric pressure, with partial anisole pressure of ≈0.048 atm. Experiments were performed at contact times (Wcatalyst/Fanisole) ranging from 0.02 to 0.17 ganisole.h.gcatalyst-1 to evaluate the deactivation. In addition, the initial porosities and acidities are evaluated by N2-physisorption, and pyridine thermal desorption followed by FTIR.

The transformation of anisole on FAU, BEA and MFI zeolites, follows an apparent first-order reaction rate equation. Regardless of reaction time, the plot of |ln(1-X0)| as a function of contact time (W/F) gives a straight line through the origin. The kinetic constants (kr, the slopes of those straight lines) decrease with time on stream (TOS), owing to deactivation, most probably through coke deposition. The deactivation functions follow an inverse exponential law, with each reaching its own steady-state reaction rate. Zeolites BEA and FAU present a much higher initial activity than MFI, with factors of more than 5 and 4 respectively between them. After a short amount of time (around 12 min), initial activities for BEA, FAU and MFI are divided by six, five and four respectively. While the higher mesoporosity of BEA and FAU, when compared to MFI would suggest a better resistance to deactivation by coke deposition, on the contrary, experiments show that the initial deactivation rate is much higher, resulting in the steady state profiles, in approximately the same timeframe. As expected, Turn-Over Frequencies (TOF) for the BEA and FAU acid sites are significantly higher than that of any tested MFI (at isoacidity, as well as with all the tested Si/Al -9 to 201- for MFI). For zeolites, and especially here MFI, the lower acid sites densities seem to produce the best TOF, indicating a higher activity of isolated acid sites, over paired (next nearest neighbors) sites, for anisole transformation.

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1060 - COPPER CONTAINING FAUJASITE AS A MODIFIER OF ANFO TYPE EXPLOSIVES

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The topic concerning the manufacture, modification, and utilization of explosives still is particularly important due to their peaceful applications. One of the most commonly used explosives is ANFO (Ammonium Nitrate Fuel Oil) due to its easy and cheap procedure of production as well as its good blasting properties.

The blasting properties of prepared explosives can undergo modification by the change of their chemical composition. It can be also realized by the addition of certain modifiers, which are able to catalyze the decomposition of explosives, reduce the emission of post-blast fumes, and influence explosive sensitivity. This action allows preparing explosives with desired blasting properties, e.g. the velocity of detonation (VOD), explosion heat, and strength or toxicity of pot-blast fumes.

In the undertaken research, we studied Cu-FAU as ANFO modifiers in terms of controlling the chemical composition of post-blast fumes due to the commonly known application of Cu-zeolites as DeNOx catalysts [1]. The choice of zeolite of FAU-type structure implies its wide application in the chemical industry due to its unique chemical and porous structures.

The FAU-type zeolite was added to the ANFO via a simple mixing procedure. Weight loading of the zeolite in the resulting ANFO-type material reached 5% wt. Prior to blending ANFO with zeolite, the parent zeolite in a protonic form (HFAU) was modified with copper (also up to 5% wt.) using a wet impregnation technique.

Analysis of either X-ray diffraction patterns and FTIR spectra indicated the presence of crystalline ammonium nitrate. The introduction of Cu-FAU to ammonium nitrate resulted in the appearance of new signals assigned to the zeolite phase. The intensity of either XRD reflexes or IR bands attributed to zeolite increased with the rising zeolite content in ANFO.

The modification of ANFO with Cu-zeolite caused significant changes in the surface of the obtained ANFO. Atomic Force Microscopy analysis indicated the appearance of numerous grains of irregular shapes assigned to the zeolite phase with simultaneous reduction of the surface folding of the prepared ANFO sample. The use of Cu-FAU decreased the thermal effect accompanying the AN decomposition from 5.82 mW/mg (for the pure ANFO) to 2.82 mW/mg.

Based on thermodynamic calculations of blasting properties, it was concluded that the application of Cu- FAU as a modifier of ANFO revealed the enhancement of the detonation properties of ANFO-type explosives, which corresponded with their changes in the status of the surface and thermal properties. It was found that in all cases, the addition of Cu-FAU to ANFO caused the growth of detonation pressure, temperature, and the heat of the explosion up to 15%, 33%, and 50%, respectively. A similar tendency was found for the VOD, which grew up to 5%. Simultaneously, the total volume of post-blast fumes (including COx, NOx, and water vapor) underwent a reduction of 6%.

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1064 - PD CONTAINING ZEOLITE CATALYST FOR DIMETHYL CARBONATE SYNTHESIS CATALYTIC ACTIVE SITES AND REACTION MECHANISM

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The shaping of catalysts is crucial for their ultimate performance at industrial level. Several shaping methods for heterogeneous catalysts are used including extrusion, spray drying, tableting and granulation. High-pressure inorganic chemistry is one of the “Top Ten Emerging Technologies in Chemistry 2020” reported by the International Union of Pure and Applied Chemistry (IUPAC). However, the high-pressure shaping of zeolite catalysts has not been investigated systematically. Particularly, the structural and chemical transformations that can take place in metal-containing zeolite catalysts under high-pressure shaping is expected to have a remarkable effect on their catalytic performance.

Dimethyl carbonate (DMC) is an environmentally friendly and sustainable compound. Recently, the gas-phase indirect oxidative carbonylation of methanol to dimethyl carbonate (DMC) has been attracting ever-growing interest due to the moderate reaction conditions, high atom economy and independence on oil. However, although this process has been successfully developed and industrialized, the experimental identification of reaction intermediates, which is of extreme importance to understand the reaction mechanism, has still not been provided to date.

This work reports on the structural changes of Pd/NaY catalysts during the mechanical compression and their impact on the catalytic performance in the DMC synthesis. It was found that the Pd valence state, dispersion and stability were sensitive to the mechanical pressure applied for shaping the catalysts. The mono-dispersed Pd clusters of 1.3 nm were obtained on the chlorine-free Pd/NaY catalyst under treatment with a mechanical pressure of 300 MPa. The Pd/NaY catalyst was highly active and stable for at least 150 h. The DMC selectivity was revealed to depend strongly on the mechanical-pressure applied, as the mechanical pressure controlled the ratio of Pd(2+δ)+ and Pdδ+ active sites ($0 < \delta \leq 2$) on Pd/NaY catalysts. Combining experimental and DFT studies, it was disclosed that the Pdδ+ rather than the Pd(2+δ)+ species enhanced the adsorption of CO and CH3ONO reactants and inhibited the decomposition of the CH3ONO reactant into byproducts, and thus enhanced the DMC selectivity.

Moreover, in situ DRIFTS experiments combined with DFT calculations provide new information on the reaction mechanism of DMC synthesis using the Pd/NaY catalyst. Two key reaction intermediates were captured by a series of steady-state, dynamic-pulse and time-resolved transient DRIFTS experiments, which were assigned to CO* (*, a surface site) and COOCH3*. It was found that the CO* intermediate is predominant on the catalyst surface when the reaction reached steady-state. DFT results also showed that the insertion of CH3O* into CO* had the highest energetic barrier of 127.5 kJ mol–1. The results suggested that the rate-determining step of the DMC synthesis is the consumption of CO*, i.e., the insertion of OCH3* into CO* thus forming the COOCH3*. The Langmuir-Hinshelwood mechanism was thus proposed, including the fast formation of CO*, and the rate-determining insertion of OCH3* into CO* toward generation of COOCH3* to yield DMC.

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1071 - UV FILTER ZEOLITE COMPOSITES PROTECTING GOODS AND HEALTH

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UV filters (UVfs) are organic or inorganic materials capable of blocking UV rays, and have become ubiquitous due to the adverse effects of UV rays on goods and human health, indeed, unprotected solar UV exposure is the main recognized cause of skin carcinogenesis. Unfortunately, organic UVfs easily undergo photodegradation, and several UVfs and co-formulants are often combined to enhance their stability and efficacy. In the last decades, the encapsulation of UV filters in diverse inorganic or organic matrixes demonstrated to be an effective stabilization strategy, e.g. [1], and the research and development of new UVfs is still ongoing. Beyond the traditional applications of zeolites, new advanced applications have been growing, also dealing with organic-zeolite hybrid materials with peculiar photochemical properties, e.g. [2].

We recently developed ZEOfilters [3], hybrid UVfs obtained by the encapsulation of octinoxate (OMC) and avobenzone (AVO) into zeolites with different topologies (MOR, FAU, MFI, and LTL) and Si/Al ratios. We optimized the loading procedure and characterized the obtained ZEOfilters focusing on their UV filtering properties.

The use of ZEOfilters should provide several advantages: i) the UVf-skin and UVf-UVf interactions should be inhibited; ii) the content of UVf, stabilizers, and other co-formulants may be reduced thanks to the enhanced filtering power and stability of the encapsulated UVfs. The optical properties of the obtained hybrids are strongly related to the UVf/zeolite combination. Potassium LTL and sodium 13X zeolites were found to be the most promising hosts for UVfs and were thus investigated more deeply. Then, as a proof of concept, LTL- and 13X-based ZEOfilters were formulated into simple cosmetic formulations.

Recently [4], selected ZEOfilters were also investigated from a structural perspective, by high-resolution synchrotron X-ray powder diffraction, Fourier-transformed IR spectroscopy, and DFT modelling. In the LTL/OMC ZEOfilter, FT-IR highlighted a perturbation of the ν(C=O) mode of the OMC carbonyl group. The structural data revealed the bonding of the carbonyl oxygen of OMC with the extraframework K cations, which is possibly responsible for the ν(C=O) perturbation in FT-IR. This interaction may also secure the UVf molecule inside the zeolite structure thus preventing its release in the environment, but this hypothesis still needs to be validated. Meanwhile, DFT calculations are ongoing, aiming to understand the behaviour of ZEOfilters based on FAU-type zeolites, which demonstrated a strongly variable properties by changing Si/Al ratio and UVf.

The observed properties are promising for the future development and exploitation of ZEOfilters, which can be a more effective, safer, and eco-friendly alternative to traditional UVfs.

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1073 - A STEP TOWARDS CIRCULAR ECONOMY REES RECOVERY FROM SPENT FLUORESCENT LAMPS EXPLOITING NH4 13X ZEOLITE CATION EXCHANGE PROPERTIES

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The demand of Rare Earth Elements (REEs) is constantly increasing due to their extensive use in many technological fields (e.g., fluid catalytic cracking catalysts, permanent magnets, batteries, fluorescent lamps), and they are considered strategic resources by the current political scenario [1]. Moreover, the monopoly of only a few countries [2], the so-called balance problem between demand and natural abundance, and the need to limit the environmental costs of their mining [3], stress the necessity of a recycling policy of these elements. Different recovery methods have been tested for REEs recovery such as selective precipitation, solvent extraction, adsorption and ion exchange. Despite the well-known ion-exchange properties of zeolites, just few preliminary works investigated their application for REEs separation and recycle. In this work we present a double ion exchange experiment on a NH4-13X zeolite, aimed at the recovery of different Rare Earths from solutions mimicking the composition of liquors obtained from a two-step leaching procedure of spent fluorescent lamps [4]. This particular waste material was chosen since it contains only four different REEs (i.e. Ce, La, Eu and Y) in two separate solutions, one with higher concentrations of Ce and La and one with Eu and Y. Preliminary exchange tests were aimed at the evaluation of the cation exchange capacity of the zeolite towards the different Rare Earths. NH4-13X zeolite was put in contact with four different mono-elemental solutions at concentration mimicking those of the fluorescent lamp liquors: Ce 0.03M, La 0.04M, Eu 0.006M and Y 0.17M. Three different solid/liquid ratios (g/ml), 1/10, 1/50 and 1/100 were tested for each solution. SEM-EDS, EA and TG analysis were performed on the so obtained powders, while ICP analysis were performed on the solutions. The results show that the zeolite was able to exchange all the REEs tested, but the exchange capacity proved to be different for the different REEs, with the higher values reported for Ce and La. This suggests a possible selectivity towards REEs. Furthermore, we observed that the higher the amount of REE in the starting solution, the higher the amount exchanged. In order to recover REEs from the zeolite a second exchange with an ammonium solution was performed. The preliminary results obtained with SEM-EDS, EA and TG analysis on the powders (only for Ce and La) for every s/l ratio tested show that almost all of Ce remains in the zeolite, while half of La is released. This once again suggests a possible selective release of REEs and open the possibility for a recovery process in which Rare Earths can be effectively separated.

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1117 - HIERARCHICAL AL AND SN BETA ZEOLITES AS CATALYSTS FOR THE CONVERSION OF BIOMASS DERIVED SUBSTRATES

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The conversion of biomass-derived substrates into high value-added chemicals is a very promising approach due to the cost-effectiveness and environmental friendliness. Isomerization and oxidation of cyclic terpenes and their derivatives as well as acetalization of aldehydes with alcohols allow to obtain fragrance and flavour substances, pharmaceutical intermediates and fuel additives [1,2]. Due to developed mesoporosity in hierarchical Al- and Sn-zeolites [3], promoting accessibility of catalytically active sites for reactants, and presence of Brønsted and Lewis acid sites of different strength, these materials can be promising catalysts in aforementioned reactions.

Hierarchical Al-zeolites consisting of beta nanoparticles were obtained via hydrothermal treatment (140 °C, 7 days) of a concentrated zeolite gel-precursor (H2O/Si = 5.5 – 15, Si/Al = 10 – 12.5) without utilization of complex structure-directing agents. Hierarchical beta (HB) zeolite with increased mesopore volume (0.94 cm3/g, Dmeso = 24±3.7 nm) and external surface area (290 m2/g) was formed at the Si/Al and H2O/Si ratios in the reaction mixture of 10 and 5.5, respectively. According to the data of pyridine ad(de)sorption monitored by FTIR spectroscopy, the half of the Brønsted acid sites in this hierarchical material (H-form, Si/Al = 12 in the sample) is strong ones (Brønsted acid sites concentration is 0.36 mmol/g, Lewis acid sites concentration is 0.22 mmol/g). Hierarchical Sn beta zeolite (Sn/Si = 15 in the sample) was prepared via a two-step post synthetic method involving dealumination of HB by nitric acid followed by wet impregnation in the absolute ethanol with the calculated amount of anhydrous tin(IV) chloride. According to UV vis spectroscopy, most of the tin atoms in the obtained sample are localized in the zeolite framework in tetrahedral coordination.
In isomerization of α-pinene (without using a solvent, 100 °C, 24 h), the conversion of this terpene and yield of the targeted product (camphene) increase (from 72 % to 91 % and from 36 % to 45 %, respectively) with increasing external surface area of the obtained hierarchical Al-beta (from 180 m2/g to 290 m2/g). Well developed external surface area of the materials improves accessibility of the active sites for reactants and increase the overall rate of the process. Application of hierarchical Al-beta in acetalization of furfural with ethanol (25 °C, 2 h) provides the highest yield of the desired acetal (up to 80%), while interaction with glycerol leads to the formation of two cyclic acetals (up to complete conversion of furfural). In Baeyer-Villiger oxidation of D-dihydrocarvone with H2O2 (30 wt% solution in water, 1,4-dioxane as a solvent, 90 °C, 24 h), 70 % conversion of this unsaturated cyclic ketone and 100 % selectivity towards corresponding lactone without formation of epoxide and epoxylactone is achieved using hierarchical Sn-beta. The selective formation of lactone can be associated with the activation of the carbonyl group of the ketone over Sn atom in tetrahedral coordination and interaction of this activated group with H2O2.

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1158 - EFFECTIVE PROTON CONDUCTION OVER THE ZEOLITE FOR HYDROGEN PRODUCTION THROUGH WATER ELECTROLYSIS AT NEUTRAL CONDITION

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Hydrogen (H2) production is a key technology to realize carbon neutrality. Water electrolysis by using an electrolytic cell including a proton-conductive solid electrolyte, in which proton (H+) resulting from water oxidation at the anode migrates to the cathode via solid electrolyte and then reduced, is a promising method to afford H2 with high purity. At the present stage, a fluorinated sulfonic polymer membrane is used as the proton conducting membrane, however, the strong acidic character of this membrane necessitates the use of acid-tolerant precious metal for the anode and the cathode. Abundant metals should be used as the electrodes for the widespread application, hence the novel H+-conductive solid electrolyte acting effectively at neutral conditions is strongly required. Regarding this, our research group reported that dealuminated beta-type zeolite possessing the silanol nests exhibited prominent H+ conductivity in pure water.[1] In this study, the H+ conduction process was detailly investigated by considering the various factor such as the amount of silanol nest and adsorbed water molecules over the zeolite surface, and water electrolysis to produce H2 was performed with the electrolytic cells involving the zeolite electrolyte in pure water. The water electrolysis efficiency strongly depended on the H+ conductivity on the zeolite. Furthermore, H2 production from the cathode was observed during the voltage application.

The zeolite was dealuminated by suspending it in the acidic solution (HCl or HNO3) and then stirred at the appropriate temperature and time. The solid after stirring was filtered and washed with water repeatedly. The resulting residue was dried at 110 °C overnight. The H+ conduction over the zeolite was investigated by the two-terminals alternating current electrochemical impedance method. A 0.15 g of zeolite was pressed to afford a rectangular column and silver paste was applied to the termini of the column. Platinum wires were coiled around the paste and then the zeolite column was immersed in pure water. Impedance was measured at 25, 45, 65, and 95 °C with the range of 0.1 Hz–10 MHz of frequency. The water electrolysis experiment was performed by using a constructed electrolytic cell consisting of Pt/C | zeolite coated membrane | IrOx/C under the application of constant voltages at 80 °C.

Arrhenius plots of the H+ conduction overt the zeolites before and after dealumination treatment indicated that the H+ conductivity was effectively enhanced by the dealumination treatment, while the proton conduction mechanism, i.e. Grötthuss mechanism, was identical for all zeolite since the activation energies were in the range of 9.6–38.6 kJ mol–1.[2] Furthermore, the H+ conduction on the zeolite surface proceeded through surface-adsorbed water molecule clusters, which was demonstrated by the dependence of the conductivity on the time of water vapor exposure. Upon the water electrolysis experiments, oxidation of water started above 1.4 V of the voltage application (overpotential: 0.22 V), and H2 was produced from the cathode. Moreover, the current density at 2.0 V increased as the Si/Al ratio became larger, indicating the dependence of the water electrolysis efficiency on the H+ conductivity. In summary, we succeeded in the H2 production via water electrolysis at neutral condition. We expect that this study become underlying technology to realize the carbon neutrality.

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1167 - CATALYTIC ACTIVITY OF YFI TYPE ZEOLITE FOR METHYLATION AND ISOMERIZATION OF NAPHTHALENE DERIVATIVES

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Reactions of polycyclic aromatics require pores larger than 12-ring. The YFI (YNU-5)-type zeolite [1] has strong Brønsted acid sites accessible through the 12-ring pore, where a naphthalene ring enters [2]. Towards efficient use of polycyclic aromatics, the catalytic activity for methylation and trans-methylation of naphthalene rings were investigated.
In dealumination, as previously reported [1], Al concentration decreased with increasing nitric acid concentration, but influence of the treatment time was small. Brønsted acid amount was always similar to [Al]-[Na]-[K], where [x] was the concentration of x in zeolite. In a flow of 2-methylnaphthalene (2-MN) + methanol mixture, dimethylnaphthalene (DMN) and 1-methylnaphthalene were mainly formed. The activity was negligible at high [Al]. High yield of dimethylnaphthalenes (DMN) was observed at [Al] = 0.5 mol kg-1, whereas 1-MN increased at low [Al]. These indicate that the catalytic activity for methylation of 2-MN was generated by dealumination, but suppressed by deep dealumination while the activity for isomerization of 2-MN was generated mainly in low [Al] region. In the flow of the 2-MN + methanol mixture, the formation rates of all methylation and isomerization products were rapidly suppressesed with time on stream, regardless of [Al]. In a flow of naphthalene + methanol mixture, 1-MN and 2-MN were mainly obtained by naphthalene methylation [3], and the degradation was also rapid. In a flow of 2-MN only (exactly, an inactive solvent cyclooctane was co-present), the isomerization of 2-MN into 1-MN was observed, and the deactivation was slow. The methylation and trans methylation (isomerization) of naphthalene ring were thus catalyzed by YFI-type zeolite, evidencing the existence of strong Brønsted acid sites accessible from the 12-ring pores [2].
Regarding the relationship between [Al] and catalytic activity, YFI was rapidly deactivated when [Al] was high. This should be due to quick carbonaceous formation on Brønsted acid sites with high density [1]. The most important findings were the catalyst degradation behaviors in low to moderate [Al] region. In a flow of 2-MN without methanol, the activity for isomerization was observed, and degradation was slow. On the other hand, the catalyst was rapidly deactivated when methanol was fed regardless of [Al] or the type of reaction taking place. The naphthalene ring must enter only the 12-ring pore, whereas methanol should enter also the 8-ring pore. It is considered that methanol became heavy carbenium ions in the 8-ring pores to deactivate the acid sites accessible from the 12-ring pores [2]. The catalyst degradation did not occur when the reactions proceeded only in the 12-ring, suggesting a potential for suppression of catalyst degradation by control of the penetration of reactants into the 8-ring pores.

In a 2-MN + methanol mixture, the isomerization selectivity was relatively high at low [Al], while increase of [Al] enhanced the reactivity of methanol for methylation. This tells us that the reaction of non-polar reactants was prior at low [Al], while the reaction related with polar compound was enhanced by increasing Al, because the electric field gradient in the pore became stronger.
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1173 - PROPANE DEHYDROGENATION TO PROPYLENE OVER PT AND GA MFI ZEOLITES

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Propylene is a highly demanded compound for the production of a wide range of chemicals, such as polypropylene, acrylic acid, etc. Its market demand has grown in recent years, but its production not, since it is mainly obtained as a by-product of the steam cracking and FCC processes. In this context, propane dehydrogenation (PDH) is considered as the most promising process for propylene production, since it could be directly obtained using propane derived from natural gas. Among the catalysts tested for PDH, Pt-containing materials exhibit a good performance, however its quickly deactivation due to coke deposition, strong sintering, poor propylene selectivity, and high cost have prompted the search for alternatives [1]. Thus, Ga-containing catalysts have also been tested in this reaction, exhibiting lower deactivation and high propylene selectivity, although their performance needs to be improved [2]. The catalysts support also has a crucial role in the catalytic performance and the regulation of its acid-base properties can be fundamental to improve the catalyst stability. Therefore, further investigation is needed in the development of efficient catalysts for PDH.

Herein, several Pt- and Ga-containing MFI zeolites were evaluated for the PDH reactions. 0.5 wt.% Pt catalysts were prepared via wetness impregnation method. To investigate the effect of the textural and acid-basic properties, Pt-modified catalysts were prepared by adding 10 wt.% of various oxides (SnO, CaO, MgO and TiO2) into the MFI zeolite before incorporating Pt. Ga MFI zeolites were synthesized via hydrothermal method with different Si/Ga molar ratios (25-40) and morphologies (nanosheet and nanosponge). In addition, Ga was also loaded into MFI zeolite by impregnation to investigate the effect of the Ga species on catalytic performance. The PDH reactions were performed in a fixed-bed reactor at 550ºC and atmosphere pressure during 4 h using 0.1 g of the catalyst. The WHSV of propane was maintained at 6 h-1 (50.8 ml/min total flow (10% C3H8, 90% N2)).

Pt-MFI zeolite showed a high catalytic activity (69% of conversion and 64% selectivity to propylene), however the excess of Brønsted acid sites (BAS) promoted consecutive reactions, resulting in coke formation, and rapid deactivation. The BET areas and BAS concentrations of the MFI zeolite were significantly reduced after the incorporation of the oxides, whereas the Pt particle sizes were significantly smaller in the Pt-modified catalysts than in the Pt MFI zeolite. Nevertheless, the Pt-modified catalysts did not show a good PDH performance. In contrast, the catalytic activity of Ga MFI zeolites increased with increasing Ga content and the tested catalysts achieved high propylene selectivity (up to 86%) and outstanding stability, likely due to the synergism between Lewis and modulated BAS incorporated by Ga atoms. These results denote the great potential of Ga MFI zeolites as catalysts in PDH reactions and highlight that the textural and acidity properties of the catalysts still need to be tuned to improve catalytic performance.

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1187 - CONVERSION OF RAPID PLASTIC PYROLYSIS GASES ON ZEOLITE CATALYSTS

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There is a demand for effective utilization of waste plastics. The current mainstream usage is to recover energy by incinerating plastics, but the environmental damage due to CO2 emissions is large. New ways to recycle waste plastics into materials or chemicals are needed to achieve a sustainable society. We thought that it might be possible to effectively recycle plastics by converting plastic pyrolysis gas into valuables by catalytic reaction. In this research, pyrolysis gas was converted using zeolite as a catalyst. In previous research, we reported that phenol can be selectively obtained by reforming the pyrolysis gas of epoxy resin used in the carbon fiber reinforced plastics over zeolite catalysts [1]. Therefore, considering that it is also effective for conversion of pyrolysis gas of plastics other than epoxy resin, in this research, we investigated the possibility of recovering valuable materials by converting pyrolysis gas of general-purpose plastics using zeolite.

Pellets of low-density polyethylene (LDPE), polypropylene (PP), and polystyrene (PS) were used as evaluation plastics. The H-BEA type (Si/Al = 18.5, 92.5) zeolite pellets sieved to 100-150 μm were used. Pyrolysis of plastics was carried out using a tandem μ-reactor (Rx-3050T; manufactured by Frontier Labs.). A reaction tube with an inner diameter of 3 mm was filled with 20 mg of zeolite pellet and both ends were fixed with quartz wool. 2.0 mg of plastic pieces were added from the upper part of the apparatus, thermally decomposed instantaneously in a thermal decomposition furnace (1st reactor) at 600 °C, and subsequently passed through a catalytic reactor (2nd reactor) at 600 °C. The products were subsequently measured using a gas chromatograph mass spectrometer (GCMS2030: manufactured by Shimadzu Corporation).

LDPE pellets were placed in a rapid pyrolysis apparatus and pyrolyzed at 600°C in the first-stage cracking furnace. As a result, pyrolysis products of various linear hydrocarbons from C3 to C35 were obtained. This was followed by decomposition at 600 °C with H-BEA type zeolite (Si/Al molar ratio 18.5) through a catalytic reactor at 600 °C to produce a mixture of propylene, benzene, toluene and xylene. Therefore, it was found that the zeolite catalyst breaks the bonds of straight-chain hydrocarbons of various carbon numbers contained in the pyrolysis gas and aromatizes them. At 500 °C or below, the pyrolysis gas is adsorbed in the catalyst and the decomposition reaction is insufficient, and the Na-type zeolite does not react at all, confirming that the zeolite acid sites are decomposing. Similar results were obtained even when LDPE was added 30 times using the same catalyst, and no carbon deposition was observed on the catalyst after the test, suggesting that the reaction was progressing stably. When PP was used, the yield of aromatic components was higher with MFI zeolite than with BEA zeolite. In PS, polycyclic aromatic compounds were obtained in the decomposition products of the catalyst.

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1194 - CARBOXYLATE BODIPY FUNCTIONAL ZINC BASED METAL ORGANIC FRAMEWORKS TOWARDS SOLID STATE LUMINESCENCE

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Boron dipyrromethenes more commonly known as BODIPYs, are molecular fluorophores that have received much attention from researchers for decades due to their high fluorescence quantum yields, large molar extinction coefficients, remarkable photo-stability and tuneable emission from visible to near infrared. Their small Stokes shift (~30 nm) is however an intrinsic limitation. Nowadays, BODIPYs are used in many applications such as bioimaging, light harvesting systems, photoactive materials… Despite excellent luminescence properties in solution, many BODIPYs suffer from the aggregation-caused quenching (ACQ) effect in solid state mainly because of intermolecular interactions such as π- π stacking, which precludes their use in luminescent materials. To address this issue, some researchers have tried to improve the aggregation induce emission effect (AIE) or to disperse BODIPYs in different matrices such as polyoxalometallates, polymers or metal-organic frameworks.

MOFs are nowadays considered as versatile self-assembled porous crystalline solid. The zinc based MOF with terephthalate ligand called MOF-5 is the most described in the literature due to its simple access and the reduce cost of precursors. Among other conditions this MOF is accessible at room temperature in a few hours using bases to accelerate the crystallization mechanism. This mild condition is compatible with organics molecules such as BODIPYs.

Herein we report a facile route, at room temperature, to integrate caboxylate BODIPYs into MOF-5 by replacing a certain amount of the ligand by the luminescent molecule. The various washes of the powder as well as leaching tests allowed to prove the good integration of the BODIPYs into the MOF structure. The small amount of BODIPYs integrated, monitored by UV-Vis kinetic follow-up, does not change the structure of the MOF-5 as proven by XRD or microscopy analyses (Fig.A). The study of the optical properties shows the conservation of the excitation and emission bands of the BODIPY in solid state (Fig.B). The measurement of the photoluminescent quantum yield (PLQY) provides good performance with values ranging from 10 to 30%. Initial thermal and photonic resistance tests have been carried out to emphasize the role of the inorganic matrices on these physical properties. Lastly, a MOF-5 like structure synthesized with zinc and a luminescent dicarboxylate ligand has been prepared. In this material the excitation of BODIPY is possible in a large part of the UV and the visible domain (Fig.C) thanks to transfer from the ligand to BODIPY. This study allows to answer the two main problems of the BODIPYs: the solid state luminescence and the small Stokes shift.

1246 - SURFACTANT TEMPLATED ZEOLITES AS BASIC CATALYSTS FOR MULTICOMPONENT SYNTHESIS

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The development of intracrystalline mesoporosity within zeolites has been a long-standing goal in catalysis as it significantly contributes to alleviating the diffusion limitations of these microporous materials.[1] In the last years, our group has described the surfactant-templating in zeolites, which allows for the introduction of tailored mesoporosity within a given zeolite, while broadly preserving its key properties such as strong acidity, crystallinity, and hydrothermal stability.[2] Moreover, we have recently reported unprecedented insights on the formation of intracrystalline mesoporosity in zeolites by surfactant-templating obtained by combining in situ synchrotron X-ray diffraction, Liquid Cell Transmission Electron Microscopy (Liq-TEM) and Atomic Force Microscopy, and Raman Microscopy.[3]

In this communication, we present the application of these novel materials in the transformation of a number of bulky molecules. Our hierarchical zeolites were previously successfully tested in petrochemical related processes,[4] and in fine chemistry related processes[5] showing, in both cases, enhanced activity and selectivity for the desired products. Here, we present how the incorporation of alkaline cations (K+ and Cs+) in surfactant-templated USY, drastically boosts its activity in the multicomponent synthesis of chromene derivatives. The resulting hierarchical catalysts combine well-defined and tunable mesoporosity, easily accessible basic sites, and the presence of siloxy-cation ion pairs (Si-O—M); yielding superior performances for the production of bulky molecules than conventional zeolites. Both conventional and hierarchical zeolites were tested as catalysts for the multicomponent synthesis of a 2-amino-chromene derivative, under solvent-free conditions. In all cases, the surfactant-templated zeolites yielded higher catalytic activity than the conventional zeolite (2-2.5 higher yield). Moreover, due to the very open structure of our catalysts, it was possible to drastically reduce the E-factor (kg waste / kg product) reported for this reaction up to values more typical of bulk chemicals production.

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1256 - PRODUCTION OF FUEL ADDITIVES FROM CRUDE GLYCEROL USING ACID ZEOLITES

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Since industrial revolution, fossil fuels have been the major source of energy [1]. However, biodiesel has become one of the most important and valuable alternative liquid fuels. For every 10 kg of biodiesel produced, about 1 kg of glycerol is formed as byproduct. So, due to continuous growing of glycerol production the actual market is unable to consume the large surplus of glycerol [2]. A potential and promising application for glycerol derivatives is the automotive sector. In particular, glycerol acetals have been identified as valuable fuel additives, solketal being of particular interest as a 100% bio-based chemical, produced from glycerol acetalization with acetone [3,4]. Zeolites, due to their excellent chemical and thermal stability, strong acid sites and industrial production, are the most promising catalysts for acetalization reactions (figure 1).

The solvent-free synthesis of solketal from pure glycerol and acetone on a batch reactor, at 25 °C, using zeolites HZSM-5 and HY with different ratios of Si/Al was the objective of this work. The best performance concerning glycerol conversion and selectivity to solketal was seen with HY60 after 10 min of reaction, 82%, and 98% selectivity to solketal. HZSM-5 50 achieved 79% conversion with 96% selectivity within 3 hours of reaction. Also the reusability of HY30 and HY60 was evaluated through 13 catalytic cycles. HY60 zeolite remained active during 13, whereas for HY30 there was a slight conversion decrease after the fifth run.

The stability of the catalysts was studied between cycles using powder-XRD and after the 6 and 13 cycle by 1H, 29Si and 27Al NMR spectroscopy. Some parameters like the presence of water in the catalysts was also studied to better understand the reaction dynamics and mechanism. At the end of this work some tests were also done using HY60 using crude glycerol, provided by PRIO-Aveiro, Portugal, collected at different points in its purification process, with very good results.

1326 - ZEOLITES SHIFT EQUILIBRIA OF TRANSFER HYDROCYANATIONS AND HYDROFORMYLATIONS

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Functional group transfer reactions are a recent family of homogeneously catalyzed reactions. They pick up a functional group (e.g. a nitrile, a formyl group) from a donor molecule and install this function on an acceptor, mostly an olefin. Transfer reactions offer the great promise that highly toxic and hazardous reactants, like HCN or CO, can be avoided in labs or industries [1]. However, the disadvantage of these isodesmic reactions is that they can be severely limited by equilibrium, especially when simple donor molecules like propionitrile or isobutyraldehyde are used. For instance, Pd-catalyzed removal of the cyano group of propionitrile to form ethylene is thermodynamically demanding and the equilibrium of the transfer reaction is largely at the left.

We here propose to shift the equilibria of these transfer reactions by adding a zeolite [2]. A well-selected zeolite irreversibly converts the olefin co-product of the transfer reaction, resulting in dramatic increases of the yield of the desired product(s). Critically, neither the olefin reactant nor the homogeneous transfer catalyst should be able to access the catalytic sites in the zeolites, while the small olefin co-product, e.g. ethylene, should be able to enter smoothly the zeolite pores. This calls for a strict control of pore sizes as a function of the co-product:

Transfer hydrocyanations: using zeolites with various catalytic functions, we introduced nitrile groups into complex substrates starting from simple donors. When using the cheap propionitrile, ethylene is the co-product; it can be in situ dimerized on a Pd-loaded ZSM-5. In the synthesis of a precursor of Lercanidipine (a heart disease drug), the zeolite induced a 54 % yield increase compared to the reaction without zeolite (Scheme, a.). Remarkably, as demonstrated by operando XAS (Scheme, b.), the Pd (added as the acetate) distributes over the phosphine ligand (in the solution outside the zeolites) and the intrazeolite sites. The effect of the Lewis acid Me2AlCl (added as a co-catalyst for the Pd-XPhos) on the zeolite was monitored by solid state NMR. When using butyronitrile or isovaleronitrile as alternative donors, strong yield enhancements are also seen; in this case, oligomerization of the propene/isobutene co-products is catalyzed by acid sites, with H-ZSM-48 emerging as a superior choice.

Transfer hydroformylations: Transfer of a formyl group from e.g. 3-methylbutanal to a reactant olefin is catalyzed by Rh/N-Xantphos, but is again limited by equilibrium. Thus, the yields of the desired aldehyde (and of the isobutene co-product) are liable to improvement. In this case as well, yields can be boosted by adding acid zeolites. It was elucidated that in this case, the acid sites predominantly catalyze the Prins condensation of the olefin co-product with excess donor aldehyde. A successful synthetic example is that of 4-(2-hydroxy-3-methylphenyl)butanal (Scheme, c.), demonstrating that the reaction possesses substantial tolerance to other functional groups, e.g. phenolic OH groups.

Summarizing, we report an original application of zeolite shape selectivity. The zeolites act in a concerted fashion with a homogeneous catalyst to improve the safety and yields of two challenging organic reactions.

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1331 - ONE STEP CONVERSION OF GLYCEROL INTO GLYCIDOL IN A GAS PHASE PACKED BED CONTINUOUS FLOW REACTOR OVER CESIUM TREATED ZSM 5 CATALYSTS

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Glycerol is a major byproduct in the biodiesel industry, accounting for approximately 10% of the total biodiesel produced. This has resulted in a decline in the commercial price of glycerol due to its overabundance in the world market. The utilization of glycerol can be performed through a gas phase over heterogeneous catalysts, producing high-value products such as acrolein, acrylic acid, dihydroxyacetone, hydroxyacetone, allyl alcohol, epichlorohydrin, lactic acid, 1,2-propanediol, 1,3-propanediol, ethanol, and glycidol [1,2]. Among these products, glycidol is highly sought after for its various industrial applications and profitability in the global market, for instance as a monomer and semi-product in the synthesis of surfactants, polyurethanes, polyamides, polycarbonates, polyesters, high-boiling polar solvents, lubricating oils, body care products, laundry detergents, disinfectants, etc. The current laboratory processes for glycidol production from glycerol have several disadvantages, including an expensive catalyst, a long reaction time, a two-step reaction process, low feedstock concentration, a liquid phase reaction, a batch-type reactor, high pressure, and the need for solvents and hydrogen donors. Our group has recently [3] developed a one-step "green" method for producing glycidol from glycerol in a packed bed continuous flow reactor at atmospheric pressure, without the use of hydrogen.

The cesium zeolite catalysts with SiO2/Al2O3 ratios of 30 and 1500 were synthesized through the wet impregnation method. The effect of Cs incorporation on the acidity/basicity and catalytic performance of ZSM-5 zeolite was studied. The structural, morphological, acidic, and basic properties of the alkali-treated zeolite catalysts were analyzed using techniques such as ICP–MS, XRD, N2 physisorption, STEM–EDX, SEM, pyridine-DRIFT, CO2–TPD, NH3–TPD, and TGA. The reaction was conducted in a laboratory Microactivity-Reference reactor (PID Eng&Tech). Usually, 0.5 g of catalyst was placed in a packed-bed tubular reactor, stabilized with glass wool on both sides. A 10 wt.% aqueous solution of glycerol was introduced into the hot box using a 307 HPLC Piston Pump with a carrier gas of N2 controlled by a mass flow controller. The temperature of the hot box and reactor was maintained at 140°C and 350°C, respectively.

The results of evaluating the catalysts showed that 20wt%Cs/ZSM-5(1500) was the most efficient in directly converting glycerol into glycidol through dehydrative epoxidation with the involvement of basic sites. This catalyst displayed high stability and selectivity, which was due to the ideal amount of basic sites and the synergistic interaction between CsNO3/HZSM-5(1500) support. It was noticed that some Si species were dissolving from the HZSM-5(1500) framework. At the same time, the glycerol conversion decreased from 86.3 mol% to 27.4 mol% in 3 hours, while the selectivity increased from 41.4 mol% to 64.3 mol% after 27 hours. The highest glycidol yield obtained was 40.4 mol% with a 10 wt.% glycerol feed, at a reaction temperature of 350°C, and total GHSV of 1250 h-1.

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1353 - IMPROVING THE RENEWABLE PRODUCTION OF NAPHTHALENES USING ZSM 5 ZEOLITE

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Naphthalenes are polyaromatic compounds, essential to produce relevant materials, such as plastics, resins, and dyes, among others. Considering their current fossil origin, their sustainable obtention is one of the main challenges of the chemical engineering. Lignocellulosic biomass is the perfect raw material for this purpose since its valorisation yields interesting platform molecules (furans, light olefins, alcohols) [1] that can be used as reactants for the aromatization by Diels-Alder reactions. This approach is evaluated in this work using ZSM 5, considering the correspondence between the zeolite porosity and the molecule size of these aromatics, according to the shape selectivity expected in this reaction [2]. A comprehensive screening of different reactant combinations was carried out, highlighting relevant conclusions, the main results being summarized in Fig. 1.

The reactions with furan/furfural + olefins/alcohols produce total conversion of the furan, furfural, ethanol and 80% in the case of using ethylene. Monoaromatics (BTXs) are the main compounds obtained (from 25 % to 40%, with furfural/ethylene and furan/ethanol, respectively) whereas the production of naphthalenes is significantly lower, the maximum value (17%) being obtained with furfural-ethanol mixture. These preliminary results demonstrate the versatile character of this approach since furfural and ethanol suffer instantaneous decarbonylation and dehydration, respectively, obtaining quite similar behaviour than when using furan and ethylene. Considering the soft conditions required to produce furfural and ethanol (aqueous phase biomass pretreatment), this mixture is identified as the optimum one to maximize the sustainability of this process. The naphthalene production significantly increases when feeding the furan compound with BTX, reaching values around 30%, decreasing the deactivation by coke as the alkylation grade of the BTX increases.

Based on these results, we propose a versatile single-stage equipment that allows the production of naphthalenes directly from green platforms: furfural and ethanol, recycling the BTX produced into the system (tertiary mixture). This configuration produces the maximum selectivity of naphthalenes (35%) with the lowest coke production of all the tested systems. Consequently, this reaction demonstrates a stability at least four times higher than the one using only furfural/ethanol mixture, a key point for a feasible scale up of this process. Moreover, the catalytic activity of the ZSM-5 is completely recovered after a thermal treatment at 650ºC.

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CATEGORY: OPERANDO INVESTIGATIONS

1010 - LOCAL OCCUPANCY IN ZEOLITE PORES INFLUENCE THE PERFORMANCE OF METHANOL TO HYDROCARBONS CATALYSTS

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Methanol-to-hydrocarbons (MTH) process is an industrially relevant method to produce valuable light olefins. Recently, it has been reported that propylene selectivity can be strongly enhanced through modification of zeolite catalysts with alkaline earth cations. [1] Here, we applied a set of transient kinetic and spectroscopic tools to understand the origin of higher propylene selectivity and overall deactivation stability of Ca/ZSM-5.

First, catalytic results demonstrate that Ca/ZSM-5, prepared by impregnation, indeed displays a higher propylene selectivity and overall methanol throughput as compared to parent HZSM-5 and reference Na/ZSM-5 catalysts (Fig. 1a). In addition, Ca/ZSM-5 possesses a much lower aromatic selectivity. In line with these results, solid state NMR spectroscopy results show that there is a significant difference in the type and amount of hydrocarbon species retained inside the zeolite pores during the reaction. 1H–13C{1H} HETCOR NMR spectrum of Ca/ZSM-5 catalyst features a much higher intensity of aliphatic peaks between 0 and 30 ppm and adsorbed methanol at 49 ppm, and DME and methoxy species at 59 ppm.

From the kinetic and NMR results we can conclude that modification of HZSM-5 with Ca cations leads to the formation of different hydrocarbon pool molecules inside the catalyst pores. However, kinetic experiments in continuous flow of methanol do not allow to distinguish molecules, actively participating in the reaction, from deactivating and spectator species. To facilitate the distinction, we performed step-response experiments, where methanol-containing reaction flow was switched to dry He. The response of catalysts to these switches was monitored by analytical and spectroscopy tools. Such experiments shed light on the structure and composition of molecules retained inside the pores during the reaction and on their mechanistic roles.[2] We found that working Ca/ZSM-5 catalyst strongly adsorbs a large number of water (Fig. 1c), methanol, DME, and aliphatic hydrocarbon molecules (Fig. 1d). In contrast, HZSM-5 and Na/ZSM-5 contain less adsorbates and these adsorbates are mainly aromatic. Combined with operando FTIR and XRD experiments, these data point to a high pore occupancy by spectator molecules in Ca/ZSM-5. These immobile species are strongly adsorbed on $Ca^{2+}/Ca(OH)^{+}$ centers and occupy as much as >10% of the microporous space during the reaction, inhibiting the formation of bulky aromatic intermediates. Absence of aromatic intermediates leads to a stronger contribution of olefin cycle to the overall reaction mechanism, higher propylene selectivity, and slower deactivation.

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1019 - OPERANDO INVESTIGATION OF [CU O CU]2+ AND [CUOH]+ SITES IN CU CHA AND CU MOR ZEOLITES FOR SELECTIVE OXIDATION OF METHANE TO METHANOL

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A mild, selective methane to methanol conversion is a major goal of modern chemistry, and this has generated considerable interest in methane-oxidizing metal sites among heterogeneous and (bio)inorganic chemists. Cu-exchanged zeolites are promising candidates for this direct methane oxidation to methanol [1]. Three zeolite topologies are particularly promising and have dominated literature since 2005: MFI, MOR and CHA. In the past, our group managed to identify and characterize a mono-(μ-oxo) dicopper(II) species ([Cu-O-Cu]2+) in MFI [2] and two slightly different [Cu-O-Cu]2+ species in MOR [3] as active sites at temperatures around 423-473 K. Recently, we added two new active sites to this catalogue of fully characterized active sites.

First, in Cu-CHA zeolites, we fully characterized a [Cu-O-Cu]2+ that is present after activation with N2O or O2 [4]. This species exhibits a clear absorption band around 22400 cm-1 in the DR-UV-Vis spectra, which decays upon methane reaction. An analysis of resonance Raman vibrations and their 18O isotope shifts obtained after activation with 18O2 was key in revealing the [Cu-O-Cu]2+ structure.

Second, in Cu-MOR zeolites, we elucidated a [CuOH]+ active site that is characterized by a broad OH− to Cu(II) charge transfer band at 20700 cm-1, a g|| = 2.27 feature in EPR and a Cu-O stretch of 750 cm-1 in resonance Raman (Δ18O = 35 cm-1) [5].

This catalogue of active sites in Cu-MFI, Cu-MOR and Cu-CHA allowed us to compare their reactivity in methane oxidation. For this, we employed operando UV-Vis spectroscopy to monitor the decay of the characteristic absorption bands of [CuOH]+ and [Cu-O-Cu]2+ during reaction with methane. The experimental results, in combination with explanatory DFT models, revealed three key elements that determine reactivity:

1) More confined locations of the zeolite lattice (e.g. side pocket in MOR) lead to a higher adsorption enthalpy for methane, lowering the apparent enthalpic barrier for H-atom abstraction (HAA) [6].
2) A coplanar orientation of the two bidentate ligations of [Cu-O-Cu]2+ to the lattice increases reactivity in Cu-CHA. These lattice-imposed geometrical constraints are reminiscent of the entatic state concept in metalloprotein chemistry [4].
3) A higher metal nuclearity leads to delocalization of the electron gained by HAA, explaining the higher reactivity of [Cu-O-Cu]2+ compared to [CuOH]+ [5].

These principles could open up new applications that require lower reaction temperatures, such as the ambient capturing of CH4 as a negative emission technology. Additionally, these structure-reactivity relationships are more generally applicable to redox catalysis over transition metal ion exchanged zeolites.

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1152 - OPERANDO IR GC MS MONITORING OF THE CATALYTIC RECYCLING OF POLYOLEFINS ON EMBRYONIC ZEOLITES

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Polypropylene, along with polyethylene, find numerous household and industrial applications as they provide cost-effective superior performances. A so far insufficient collection of these and all non-biodegradable plastics generates an unsustainable amount of severe pollution; marine plastics pollution being the highly visible tip of this iceberg. Currently, only 16 % of plastics waste is reprocessed to make new plastics with only about 1% chemically reporcessed to provide the original (olefinic) building bocks, i.e. a true circular economy. So a large proportion of plastics is either left in nature, landfilled, mechanically recycled or incinerated. Catalysis has a role to play to solve such an important societal challenge.

Zeolites are some of the most important heterogeneous catalysts in oil refining and petrochemistry due to unique properties such as high surface areas, well-defined topology with uniform micropores, shape selectivity, numerous and strong acid sites, high thermal as well as chemical stability. Their micropores confine adsorbates and reactants leading to exceptional selectivities in separations and catalytic processes. The downside however is the presence of severe diffusion limitations resulting in a partial use of all their potential “active” sites when bulky molecules are involved. One of the earliest explored remedy is the design of hierarchical zeolites where mesopores are added post-synthesis to their pristine micropores. Another approach is to synthesize small zeolite with crystals, the so-called nano-zeolites. Another promising approach is to synthesize embryonic zeolites (EZ); these X-Ray amorphous materials, harvested in the early steps of a zeolite synthesis, lack the long-range order of zeolites but their active sites are more accessible enabling the conversion of bulky molecules such as 1,3,5 – triisopropylbenzene. EZ therefore extend the range of applications of current zeolites to the processing of heavy oil fractions and related feedstocks such as polyolefins.

We report the catalytic cracking of polypropylene on a microporous ZSM-5, a hierarchical desilicated derivative and an embryonic ZSM-5, i.e., a material that upon longer hydrothermal treatment would yield a fully crystalline ZSM-5. Both EZ and the hierarchical ZSM-5 have close Si/Al and therefore similar number of Brønsted acid sites and textural (Smeso) properties. Polypropylene and polyethylene conversions are monitored by operando FT-IR coupled with CG-MS to simultaneously measure catalytic activity, deactivation and product selectivity.

On the EZ, polypropylene produces the lowest C3-C4 (gaseous) and C5-C6 (liquid) fractions but more of the C7+. than the two ZSM-5 catalysts as the lower confinement in micropores prevents secondary cracking. Moreover, a high hydrogen-transfer in EZ, related to its textural properties, provide a much higher paraffin (70 %) selectivity compared to the zeolites. The H2 captured in the light paraffinic fraction can be recovered by catalytic dehydrogenation leading also to valuable lower olefins. 2D COS IR spectroscopy monitoring of coke formation and combustion highlight the role of silanols in the coke retention. Rapid Scan FT-IR spectroscopy of neopentane diffusion brings more insight on the diffusion by the application of the Crank method.

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CATEGORY: SEPARATIONS

1047 - A COMPREHENSIVE DYNAMIC SEPARATION OF CO2 N2 USING NANOSIZED CHABAZITE ZEOLITE COMBINED EXPERIMENTAL AND THEORETICAL STUDY

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Flue gas composed of CO2, N2 and others is a major by-product of gas treatment, refineries and power plants. Due to the increasing atmospheric concentration of CO2 from anthropogenic sources, the separation of CO2 from N2 is a crucial priority. Four technologies are currently employed for CO2 capture: (i) adsorption with amine-based solvents, (ii) adsorption by nanoporous solids, (iii) cryogenic distillation, and (iv) membrane separation. Amongst the materials considered for CO2 adsorption, zeolites have the advantage of being inorganic non-toxic materials with high thermal stability and selectivity that can be tuned by their framework structure and chemical composition.[1] Conventional zeolites suffer from diffusion limitations of guest molecules through their pore networks as they are typically composed of micron-sized polycrystalline particles.[2] Several methods have been developed to overcome these limitations by increasing the surface area/volume ratio. Among different materials, nanozeolites composed of discrete nanoparticles (single crystals) giving rise to a greater external surface area and accessible active sites.[3]

We have demonstrated the excellent CO2 capture properties of different alkali forms (Na+, K+, and Cs+) of nanosized chabazite (CHA) zeolites and the use of classical physics calculations for predicting adsorption isotherms.[1]

In this work, firstly the CO2 and N2 equilibrium adsorption isotherms were predicted by Grand Canonical Monte Carlo (GCMC) calculations at 298 K. Using molecular dynamics simulations, self-diffusivities of CO2 molecules with various loadings were estimated for different alkali forms of CHA nanozeolites. Finally, the dynamic separation of CO2/N2 was verified experimentally by breakthrough measurements using gas mixture with a CO2/N2 of 17/83 at 298 K. The CO2 loadings of 2.48, 1.72, and 0.57 mmol g-1 for Na-, K-, and Cs- CHA nanosized zeolites based on breakthrough measurements were obtained. The CO2/N2 molar selectivities of 62, 46, and 48 for the three samples Na-, K-, and Cs- CHA, respectively were measured. The dynamic CO2/N2 selectivities were in a good agreement with the simulated data using GCMC and molecular dynamics proving the efficacy of the methods in predicting the adsorption of different gasses in zeolite. Different alkali forms of nanosized CHA zeolites prove to be excellent materials to separate CO2 from N2.

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1070 - MIXTURE EQUILIBRIUM DATA FROM INTERMEDIATE PLATEAUS OF BREAKTHROUGH CURVES ALCOHOLS ON ALL SILICA BEA ZEOLITE

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The use of microporous materials such as zeolites, with cavities having the size of guest molecules, is well known to accomplish molecular separations via adsorption. While pure gas adsorption measurement techniques being established and often highly automated, measuring multicomponent equilibria remains challenging. These mixture adsorption equilibria are of very large interest to the zeolite, catalysis and adsorption communities and essential in the development of adsorptive separation processes. Unfortunately, such data remains hard to come by even though a variety of experimental measuring techniques is available[1]. In this context, Shade et al. [1] note that breakthrough methods are amongst the most used techniques to obtain such mixture data. A breakthrough curve is collected by applying a step in concentrations at the zeolite column inlet and measuring the concentration changes at the outlet. Typically, the curves are integrated to complete breakthrough for the missing mass, thereby yielding the adsorbed amounts in equilibrium with the feed. This yields one equilibrium point for each breakthrough test, which can be both time-consuming as labour-intensive. Remarkably, breakthrough curves often present themselves as a series of constant concentration (plateau) regions, separated by mass transfer zones. Beyond the obvious initial and final plateaus, intermediate concentration plateaus then emerge. This includes the so-called ‘roll-up’ phenomenon where the less strongly adsorbed component can be displaced from the zeolitic structure by the other components, causing a temporary overshoot of the feed concentration, stabilizing at an intermediate concentration level. By replotting the experimental time-dependent data, a simple graphical tool is presented to yield equilibrium data from those intermediate plateaus. No model fitting or pure component isotherms are required. This allows to obtain two mixture equilibria points from one (binary) breakthrough test, and even more when more complex (ternary, etc.) mixtures are used. The technique is demonstrated numerically and discussed from theoretical point of view. Next, the technique is demonstrated for the adsorption of various alcohols on an all-silica BEA zeolite. For this zeolite, pure component alcohol isotherms are known to be S-shaped due to the hydrophobic behaviour of the zeolite[2], and give rise composite (shock and dispersive) breakthrough waves. In this work, adsorption of methanol/ethanol and ethanol/isobutanol mixtures is studied, with and without preloading the zeolite column, to obtain multiple equilibria points from one breakthrough tests.

The graphical method could be verified numerically (beyond binary) and (binary) experimentally, where two or more validated equilibrium points can be extracted from a single breakthrough curve. The method offers practitioners an extra tool to verify their breakthrough tests with e.g. static pure component isotherm test, or increase the experimental output from their breakthrough methods.

1083 - ORGANO FUNCTIONALIZED SILICAS FOR SELECTIVE SOLID PHASE EXTRACTION OF CRITICAL MATERIALS

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Growing population, rising energy consumption and increase production of high and modern technology devices significantly increase the global consumption rate of rare earth elements (REEs). In industry, separation and purification of REEs is mostly done via liquid-liquid (LLE) or liquid-solid (SLE, SPE) separation methods. [1,2] Yet, both techniques are hampered by several limitations i.e., insufficient selectivity, ow reusability rate or high costs of the chromatographic resins used. Moreover, currently existing procedures often require large quantities of solvents and water, subsequently generating huge amounts of undesirable wastes. In addition, due to very similar physio-chemical properties of lanthanides the extraction procedures have to be repeated several times to obtain high purity fraction of lanthanides suitable for further applications. Consequently, efficient and selective REE extraction/purification, in an economically and environmentally effective manner, remain a tedious task. In that perspective, the development of efficient, selective and reusable sorbents is urgently desirable.

Among various complexing agents used for the lanthanide separation, the diglycolamide (DGA)-type ligands have attracted the highest attention, particularly in LLE processes. Consequently, their extraction behavior and complexation properties are widely studied. However, the extraction behavior of the DGA ligands is not extensively investigated when such ligands are tethered to a solid support. A detailed understanding of the relationship between chemical structure and extraction behavior, at the molecular level, is still missing in the literature, even though it is a crucial factor in the development of efficient solid-phase sorbents. In addition, profound knowledge about interactions taking place on the surface of solid-phase sorbents may also reduce the costs associated with trails experiments and material design.

In our studies, we used diverse spectroscopic techniques (e.g., solid-state NMR, X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy) to obtain comprehensive knowledge about DGA functionalized mesoporous silica (KIT-6) sorbents and their extraction behavior. [3] Based on our results, it can be suggested that depending on the extracted element, structure of the ligand or its pre-organization on the silica support, different functional groups (i.e., C═O, N–H, or silanols) act as adsorption centers leading to different complexation preferences of the obtained sorbents and consequently to different extraction mechanisms. This various extraction behavior may be related to the differences in the size of the ligand, precisely to the size of the chelating bite angle, amount and accessibility of the chelating ligand, density of 'free' silanol groups, or even to the local surface environment.

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1085 - IMPACT OF PORE STRUCTURE OF CHA AND GIS ZEOLITES ON GAS ADSORPTION SEPARATION

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Currently up to 15 % of the world energy consumption is related to different chemical mixture separations [1]. Gas separation is among the most important and widespread industrial processes which includes natural gas purification, post-combustion CO2 capture, H2 recovery from purge gases and O2/N2 separations, which are used for bio-medical applications. Therefore, there is a need to create novel, cheap, sustainable adsorbents for the highly effective process of separation with high performance and low energy demand.

In this regard, small pores zeolites are perfectly well suited for the adsorption and separation of small molecules (H2, N2, CO2, CH4, etc.) since the free aperture (0.30–0.45 nm) of the 8-membered rings (8MR) are geometrically corresponding to the adsorbate's kinetic diameters [2,3]. Moreover, their adsorption and separation properties can be precisely tailored by changing extraframework cations of the as-synthesized zeolites. Substitution by large monovalent cations (such as K+, Rb+, Cs+) will increase the separation efficiency by trap/swing-door mechanism, whereas substitution by small divalent cations (such as Ca2+, Mg2+, Zn2+, etc.) increase available microporous volume in the zeolite framework for an adsorbed gas molecule and could possibly lead to an increase of the effective gas adsorption capacity due to specific interactions between adsorbed molecules and cationic sites.

The proposed work focuses on two zeolites being built from the same unit blocks but exhibiting two different final pore structures: chabazite (CHA) and gismondine (GIS. The CHA framework is formed by hexagonal prisms, stacked in layers and linked by tilted 4-membered rings (MR). It is characterized by a 3D pore system with [4126286] ellipsoidal shaped cages of 6.7 × 10 Å2 interconnected via 8MR windows (0.38 × 0.38 nm2). The GIS zeolite is composed of two orthogonally connected double crankshaft chains, which form 10-hedral [4684] cages with four 8MR openings (0.31 × 44 nm2) in [100] and (0.26 × 0.49 nm2) in [010] forming an interconnected channel-like system. The absence of 6MRs and hexagonal prisms in the GIS structure combined with the differences in the geometric parameters of the 8MR windows are of particular interest respective to the adsorption performance, especially when considering various divalent extraframework cations. To rationalize and quantify the importance and extent of these effects, we propose a systematic study combining both synthesis and thorough characterization of micro- and nanosized zeolites of CHA and GIS topology with variable Si/Al ratio (1.9–3.0) and different counter cations (Na+, K+, Zn2+, etc.). The influence of the zeolite topology, the particle size, Si/Al ratio, as well as the nature and loading of the extraframework cation on small gases (H2/N2/CO2/CH4) adsorption capacity was analysed in details by high-pressure (up to 200 bar) single component adsorption. The gas chemisorption was studied by in-situ FTIR gas adsorption. Finally, realistic gas separation efficiency was investigated by dynamic column breakthrough adsorption experiments.

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1087 - SI O C CROSS LINKING BETWEEN ZEOLITE NANOPARTICLES AND GO IN COMPOSITE MEMBRANES TO TRIGGER HIGH PERMEANCE SELECTIVITY AND STABILITY IN GAS LIQUID SEPARATION

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Zeolites with uniform pores and stable frameworks are ideal candidates to build molecular sieving membranes. Framework structures such as zeolites (LTA, CHA, and MFI) with pores constructed of 8-membered rings (8MR) or larger (10MR), have been widely studied as components of membranes for both gas and liquid separations. At present, the biggest bottleneck in the development of zeolite membranes is the preparation technology of large area continuous and compact zeolite membranes, which is hindered by the difficult control of zeolite nucleation and subsequent crystal growth on the surface of the substrate.

An ideal situation is developing an appropriate dense surface creating an accessible zeolite porous framework with pores similar in size to the target molecule. Very recently, Graphene oxide (GO) nanosheets are commonly produced by exfoliating graphite under strong oxidizing conditions, thus producing many carboxylic acid and phenolic hydroxyl groups, which offering highly reactive to form stronger interactions with zeolites. Furthermore, GO can be readily dispersed in water, forming stable GO colloids, which is conducive to the preparation of laminated GO membrane. It is expected that the zeolite/GO hybrid membrane due to the unique molecular transport of GO sheet will contribute to the enhancement in the water gas/liquid permeability, whereas the zeolite component will contribute to the high selective of gas/liquid separation.

Herein, the GO/zeolite hybrid membranes were prepared by direct transformation of infiltrated amorphous precursor nanoparticles, impregnated in a graphene oxide (GO) matrix, into zeolite (EMT/SOD) nanocrystals. The FT-IR results shows the amorphous precursor particles are rich in silanols (Si-OH), which enhanced the interactions with the GO and led to the formation of highly adhesive and stable zeolite/GO membranes via strong bonding. The XPS result has verified the formation of Si-O-C bond and the crosslinking between the GO and zeolite nanocrystals. The cross-linking of zeolite nanoparticles with the GO in the membranes promoted both the high gas/liquid permeance and enhanced selectivity. The SOD/GO membranes with small pore size are moisture resistance and exhibit steady separation performance (H2 permeance of about 4900 GPU and H2/CO2 selectivity of 56, with no degradation in performance during the test of 50 h) at high temperature (200 °C) under water vapor (4 mol%). While, under the reinforcement of the crosslinked bond (Si-O-C), the hybrid GO/EMT with the big pore size membrane exhibited higher dye removal rate than GO membrane with long-term stability. In addition, this membrane could also be used for heavy metal ion removal.

1105 - INVESTIGATING THE POTENTIAL OF MOF 808 BASED ADSORBENTS FOR LIGHT OLEFIN PARAFFIN SEPARATIONS

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Light olefins, such as ethylene and propylene, are highly demanded feedstocks in the chemical and petroleum sector and used mainly to produce polymers [1,2]. These olefins are recovered from process streams containing different concentrations of their paraffin counterparts. Currently, cryogenic distillation processes are applied for their separation and purification at a large scale. These processes are energy-intensive, owing to the similarity of physical and chemical properties of the hydrocarbons. Therefore, efficient separation process alternatives, such as membranes, need to be developed to reduce the associated carbon footprints [2, 3]. Ideally, a membrane process should offer high selectivity, permeability, processability, and stability [4]. The class of mixed-matrix membranes (MMMs), containing a selective polymer and metal-organic framework (MOF) fillers, can enable the desired tuning of permeability and selectivity, due to the subtly engineered combination of kinetic and equilibrium effects in the polymer matrix and embedded porous solid particles [5,6]. MOFs are known for their versatile, porous crystalline structure; and their chemical properties can be tuned to address these challenging separation tasks. Tunability of pore sizes and functionalities in MOFs can be exploited to separate gases based either on their size, shape, or binding type [2]. MOF-808 is a Zr-based MOF having a large surface area and pore volume. It provides a versatile and stable platform for adapting functionalities into its framework due to coordination sites on its Zr-clusters [7]. In the current study, the adsorptive features of MOF-808 and several kinds of functionalized MOF-808 materials are investigated to evaluate the effect of functionalization on the adsorption properties and assess their viability as fillers in MMMs. We conducted pulse inverse gas chromatography (IGC) and adsorption isotherm measurements to determine adsorption thermodynamics, including Henry coefficients, thermodynamic selectivity, isosteric heats of adsorption at infinite dilution, and adsorptive capacities of C2/C3 species. The results show that certain functionalities can improve MOF-808s selectivity for the unsaturated molecules. The heats of adsorption of C3s increased slightly after the functionalization of MOF-808. In the low-pressure range, the adsorption capacities of modified MOFs are higher compared to the pristine MOF. The results of this study offer perspectives for the design of MMMs with remarkable separation potential for light olefin/paraffin mixtures.

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1245 - DEVELOPMENT OF ROBUST ADSORBENTS WITH BALANCED BINDING AFFINITY FOR AMBIENT NO2 ADSORPTION

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Anthropogenic emissions of various toxic gases cause serious environmental problems and pose substantial health threats. One typical example is Nitrogen dioxide (NO2) generated from the burning of fossil fuels at power plants and vehicles. Its emission leads to acid rain, the formation of PM2.5 and tropospheric ozone. Human exposure to NO2 and its derived pollutants readily causes various respiratory diseases. Mitigating the adverse impact of NO2 requires effective gas treatment technologies – gas detection, removal, and conversion, which can be nicely enabled by selective gas adsorption in porous solids. The key to an effective gas adsorption operation is to have porous adsorbents capable of affording high selectivity, high capacity, high stability, and high regenerability. High adsorption selectivity and capacity assure effective enrichment of target toxic gases in adsorbents, while high stability and regenerability assure multiple reuses of adsorbent materials. Given its corrosive and destructive nature, effective NO2 adsorbents should feature specific binding sites capable of imparting balanced affinity to assure highly selective NO2 uptake of appreciable amount on one hand, and to assure regenerative adsorption and material stability on the other. However, few adsorbents can satisfy these requirements.

In this talk, I will present our attempts to develop effective adsorbents for NO2 adsorption at ambient temperature in recent years. Our study on the effect of basic sites, i.e., either metal oxide or metal hydroxide moiety as basic sites in layered double hydroxides and their derived mixed metal oxides featuring, showed that such a strong acid-base interaction can afford high NO2 capacity but inferior regenerability and material stability [1,2]. Our exploration on an ultrastable MOF, i.e., DMOF featuring the absence of strong binding sites and hydrophobicity, realized a stable cyclable NO2 adsorption but of inferior capacity. To reach a balanced binding affinity, we resorted to π-backbonding interactions enabled by appropriately tailored transition metal species in various adsorbent supports, such as various copper species on high surface area silica [3], various copper species in metal-organic frameworks derived carbons, various transitional metal cations in zeolites, various transitional metal cations in covalent triazine frameworks [4], various transitional metal cations in porphyrin metal-organic frameworks [5,6]. We conclude that engineering transition metals as specific adsorption sites of appropriate binding affinity is a promising strategy to develop NO2 adsorbents, which could be extended to other corrosive and toxic gases.

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1346 - SCALING UP OF ZEOLITE MEMBRANE MANUFACTURING FOR NATURAL GAS TREATMENT IN INDUSTRIAL SCALE

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Zeolite ZSM-5-membranes are ideal for the continuous and energy efficient separation of organic solvents from water[1], branched from non-branched hydrocarbons[2] or higher hydrocarbons from natural gas[3]. Zeolite SAPO-34 membranes of great interest for CO2/CH4-separation. However, for industrial application the synthesis of zeolite membranes must be scaled-up in terms of membrane geometry and manufacturing technology.

Zeolite membranes were prepared by slurry coating for seeding, hydrothermal crystallization and detemplating at 450°C on ceramic support tubes. For ZSM-5 membranes in first step ceramic supports with a length of 250 mm and an increasing number of channels (1, 4, 7, 19 channels) were used. The success of the synthesis was checked by PV-separation of ethanol from water (5 wt% ethanol) at 40°C.

In a second step, 15 membranes with a length of 600 mm and in 19-channel geometry were synthesized in a single batch. Two batches were run. The membranes were examined using permporometry to check the defect rate in zeolite layer. Real natural gas was used for testing the separation of n-butane at 25°C. In case of SAPO-34 in first step the length of single channel tubes was increased step wise from 100 mm up to 500 mm. In a second step reproducibility and membrane quality was improved. All membranes were characterized by single gas permeation and mixed gas separation in 0.5 CO2/0.5 CH4-mixtures.

In PV tests with ZSM-5 membranes prepared on ceramic supports with different numbers of channels all membranes showed a clearly hydrophobic separation behaviour and were able to prove their functionality. Two 600 mm long membranes in 19-channel geometry from each synthesis batch of 15 membranes were examined using permporometry. It was found that all membranes achieved a defect rate of <1%. With three membranes, the value was even 0.1%. In natural gas for all tested membranes (28 elements) high permeance of in average of 3.9 $m^3/(m^2hbar)$ = 4.9 10-7 $mol/(m^2sPa)$ and high n-butane/CH4-selectivity of 24 was found. In some cases, all n-butane was separated from the natural gas and a highly concentrated stream containing 60% n-butane was recovered.

Excellent CO2/CH4 selectivities of around 200 were found for SAPO-34 membranes on 105mm long tubes in single and mixed gas permeation. However, simply increasing support tube length reduced selectivity down to 30. Synthesis optimization enabled membranes with CO2/CH4 selectivities of around 250 to be produced on both 250mm and 500mm long support tubes with best selectivity of 1,250.

Excellent ZSM-5 and SAPO-34 membranes in increased geometry and batch size are available for separation tasks in the field of natural gas processing.

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CATEGORY: STRUCTURE CHARACTERIZATION

1015 - HYDROGEN ACTIVATION ON MOLECULAR MOLYBDENUM SULFIDE CLUSTERS ENCAPSULATED WITHIN THE PORES OF NAY ZEOLITES

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Transition metal sulfides (TMS) have played an important role in industrial catalysis for over a century. Being ubiquitously utilized for heteroatom removal from petroleum feedstock, these catalysts have made their way into a multitude of other processes such as upgradation of bio-derived feedstock, reverse water gas shift reaction, CO₂ conversion, and more recently in electrocatalytic H2 evolution. Such is the importance of these TMS phases that nature has also found a way to incorporate these active phases into its own catalysts: <i>the enzymes</i>. The active site in the nitrogenase enzyme, commonly referred to as the FeMo cofactor, has been identified as a Fe-Mo sulfide cluster.

Industrial TMS catalysts, typically composed of sulfides of Mo or W, are often promoted with the addition of other 3d transition metals (most prominently Ni and Co). These mixed metal sulfide catalysts exceed the activity of monometallic Mo or W sulfide catalysts by a wide margin. Interestingly, different mixtures of base and promotor metals result in a particular enhancement of individual reaction types.

As a large fraction of reactions investigated on these TMS catalysts involve H₂ as a reactant, a significant amount of effort has been put into understanding H₂ activation on these materials. It is widely accepted that H₂ activation on these catalysts occurs via dissociative adsorption followed by stabilization of hydrogen as either sulfhydryl (–SH) groups or as hydride species.

With the aim of improving the fundamental understanding the hydrogen activation in zeolite-encapsulated mixed TMS clusters, we have combined kinetic studies with operando spectroscopy and density functional theory (DFT) calculations to understand the mode of hydrogen activation on the zeolite-encapsulated mixed TMS clusters.

Zeolites are ideal supports for forming well-defined TMS clusters due to their stable and structurally well-defined porous framework. We have recently synthesized homogeneously distributed molybdenum sulfide clusters encapsulated in the micropores of NaY. The tetrameric Mo₄S₄ clusters electronically and structurally resembled the cubane motifs of the FeMo-cofactor and exhibited remarkable stability for ethene hydrogenation, while the classic layered MoS₂ catalyst deactivated significantly under the same conditions.

These promising results motivated us to address, how these clusters activate and stabilize H₂ and how their structures dynamically adapt to the reaction environment. Combining IR spectroscopy with kinetic measurements and DFT calculations we showed that the zeolite-encapsulated molecular MoxSy clusters primarily activate and stabilize H2 as hydride species on Mo atoms while the bulk TMS phase stabilizes hydrogen primarily as sulfhydryl (–SH) groups.

With the aim of further improving the molecular understanding the H₂ activation in these zeolite-encapsulated TMS clusters, we have investigated how the mode of H₂ activation varies based on their composition. Partially ion-exchanging the NaY zeolite with Ni²⁺ or Co²⁺ resulted in the formation of interconnected mixed TMS phases. Their structure was elucidated <i>via</i> a combination of <i>in situ</i> XAS and DFT calculations. Further combining theory with IR spectroscopy, we could show that the S-atoms bridging the two sulfide phases provide a new site for hydrogen stabilization as –SH groups, in addition to the formation of hydride species. This additional path for hydrogen activation resulted in improved activity of these mixed TMS clusters for ethene hydrogenation.

1022 - DIRECT LOCATION OF GUEST MOLECULES IN POROUS CRYSTALLINE MATERIALS BY THREE DIMENSIONAL ELECTRON DIFFRACTION

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Understanding host-guest interactions is one of the most important tasks in the study of open-framework materials, such as zeolites, metal-organic frameworks (MOFs), and covalent organic frameworks (COFs). As it offers us fundamental knowledge of the materials in gas sorption, separation, catalysis, etc., probing host-guest interactions, especially at an atomic level, is crucial for revealing the unique properties of the open-frameworks and identifying their roles in various applications.

To locate guest species and study host-guest interactions, single crystal X-ray diffraction (SCXRD) is the conventional method. However, incorporation of guest molecules often causes cracking on large crystals, which hinders structural analysis by SCXRD. Three-dimensional electron diffraction (3DED) has been developed as a complementary technique for single crystal analysis of tiny crystals1. Because only a small piece of crystal is needed, it therefore opens new opportunities to tackle the drawback when crystals are damaged. Furthermore, small crystals facilitate diffusion which increases the occupancy of guest molecules in the pores for detection. Although powder X-ray diffraction (PXRD) could also provide crucial information about guest molecules, its accuracy is often sensitive to the challenges in PXRD analysis, such as peak overlapping and presence of impurity.

I will talk about our recent development on direct location of guest molecules in two open-framework materials, SU-8 and SU-68 by using 3DED2. Notably, with low electron dose and ultrafast data collection, we demonstrate for the first time that the guest molecules can be identified as distinct and well-separated peaks in the difference electrostatic potential maps showing a high accuracy and reliability comparable to SCXRD. As a result, two different spatial configurations are identified for the same guest molecule in SU-8. In addition, we find that the guest molecules interact with the framework through strong hydrogen bonding, which is the key to immobilize the guest molecules at well-defined positions.

Our study shows that 3DED not only provides accurate framework models as those obtained by SCXRD, but it also represents a reliable method for probing host-guest interaction at an atomic level. Considering the difficulty in obtaining large crystals and keeping their high-quality after introducing guest species, we foresee that electron diffraction will increase its importance in studying host-guest interactions in open-framework materials, such as MOFs, COFs and zeolites.

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1023 - SYMMETRY BASED RECOUPLING IN 29SI NMR TO PROBE HETEROATOMS IN ZEOLITES A COMBINATION OF EXPERIMENTAL AND THEORETICAL APPROACHES.

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Tuning the location of acid sites in zeolites' catalysts would allow the control of their acidity to enhance the yield of a specific reaction [1]. However, the distribution of heteroatoms is still challenging many researchers around the world since the experimental methods used for their localization, either spectroscopic (Nuclear Magnetic Resonance (NMR) and Infrared (IR)) or diffraction-based (Electron, neutron and X-ray) approaches, are reaching their limits in terms of resolution nowadays [2].

29Si NMR spectroscopy was the first to be explored in zeolites thanks to the pioneering works of Engelhardt and co-workers giving a robust and simple way to assign silicon sites differing in their coordination state and consequently their isotropic chemical shifts. These studies resulted in many structural-spectroscopic correlations allowing a clear understanding of zeolites structures at the atomic level [3]. Although the substitution of Si by Al is possible thanks to the similarities in size and electron density of both atoms, the peaks' assignment of the corresponding spectra is still a complex task even with the help of DFT calculations, especially when structures with many overlapping non-equivalent tetrahedral sites are examined [4].

Moreover, a wealth of precious structural information is held by anisotropic interactions that are often averaged out by magic angle spinning (MAS) hindering their direct determination while enhancing the spectral resolution. To keep the advantageous resolution in the spectra and get access to the anisotropic interactions, symmetry-based recoupling techniques were introduced twenty years ago allowing the introduction of anisotropic interactions selectively [5].

In this contribution, we show a complete methodology using a combination of (i) homo- and hetero-nuclear symmetry-based recoupling techniques in 29Si NMR, (ii) spin dynamics-based simulations and (iii) DFT based theoretical calculations, how the nature and location of heteroatoms could be disentangled in highly ordered, defect-free nanosized ZSM-5 zeolites.

Acknowledgments

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1031 - P INDUCED CRYSTAL FLUID INTERACTION IN 6 MEMBERED RING ZEOLITES THE CASE OF ERI OFF AND EAB TOPOLOGIES.

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Pressure (P)-induced intrusion of molecules (or solvated ions) into the structural nano-cavities of microporous materials opened a new route to promote a mass transfer from fluids to structurally-incorporated molecules. A full understanding of this phenomenon in natural or synthetic zeolites might expand the number of their utilizations, e.g. tailoring of new materials, as catalysts in industrial processes [1,2]. On the other hand, from the geological point of view, the study of this phenomenon is unveiling the role played by zeolites as fluid carriers in the upper Earth crust, e.g. during the early subduction of oceanic sediments or altered basalts.
We have investigated the high-P behaviour, promoting P-mediated crystal-fluid interaction, of three different zeolites with structural homologies: erionite (ERI framework type, 6-membered ring sequence: AABAAC), offretite (OFF, with AAB seq.), bellbergite (EAB, with AABCCB seq.) and its synthetic counterpart. These studies allowed to 1) a better understanding of the potential role played by erionite as fluid carrier during the early subduction, being this mineral a constituent of ocean floors basaltic alteration [3] and 2) compare the mechanisms adopted by structurally similar 6-mRs frameworks to accommodate the bulk compression and the crystal-fluid interactions.

Synchrotron X-ray diffraction experiments have been performed on natural single crystals of erionite, bellbergite and offretite. Additionally, experiments have been performed on powder samples with EAB framework (synthetized according to the Aiello-Barrer protocol [4] and treated in order to obtain Na- and K- forms). Both non penetrating (silicone oil and daphne oil 7575) and potentially penetrating P-transmitting fluids (methanol:ethanol:water 16:3:1 mixture, ethanol:water 1:1 mixture, methanol, H2O, liquid Ne) have been used.

Among the natural samples, erionite resulted to be the one with the highest magnitude of adsorption. The new adsorbed molecules act as “pillars” within the framework nanocavities, decreasing the compressibility of the structure. Moreover, the magnitude of the intrusion resulted to be strictly related to the H2O content of the hydrous P-transmitting fluids.

Ne atoms were able to penetrate into the 12mRs channel of the offretite framework in response to the applied pressure, with weak Van der Waals interactions with the extra-framework population.

Methanol resulted to behave as a non-penetrating fluid for natural bellbergite, while it acts as a penetrating fluid in the synthetic counterparts. This highlighted the role of “secondary factors” on the occurrence of crystal-fluid interaction, e.g. the extra-framework content of the sample and the size of crystallites (single crystal of natural bellbergite vs. synthetic EAB powder).

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1049 - RELATION BETWEEN A ZEOLITE MICROSTRUCTURE AND ITS SILVER LOADING FOR AN OPTIMIZED XENON ADSORPTION

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In molten salt nuclear fission reactors, a mixture of molten salts is used as fuel but also as the primary coolant. During its operation, fission products, such as krypton and xenon, are generated within the reactor and must be recovered and stored. Selective capture of Xe can then be achieved using solid supports in fixed bed processes. Silver loaded ZSM-5 zeolites have been identified as excellent materials for this application because they have both a high Xe capture capacity and an excellent Xe/Kr selectivity [1, 2]. However, it has been shown a decrease of their adsorption performances in presence of chlorinated species (possibly formed into molten salts reactors) or after their reuse, due to the sintering of Ag nanoparticles, which are strong Xe adsorption sites at low pressures [3]. In this context, the objective of this study conducted by the CEA and ORANO is to better understand the relation between the microstructure of a ZSM-5 zeolite and its silver loading in order to synthesize more efficient and stable materials. For that purpose, zeolite particles with different levels of structural defects were synthesized by desilication of a reference ZSM-5 zeolite. The controlled elimination of Si results in the creation of silanol-type defects as well as the formation of mesopores. These materials were then loaded with silver by cationic exchange and the Ag speciation as well as the distribution of Ag nanoparticles after thermal treatment were finely characterized coupling transmission electron microscopy and ultraviolet-visible spectrocopy. Indeed, the thermal treatment creates dispersed fine Ag-nanoparticles, which can possibly be stabilized by silanol defects. A short desilication time induces the elimination of extra-framework Al and the presence of a mesoporous network, leading to the integration of a higher amount of Ag in the material by promoting the accessibility of exchange sites. The fine Ag particles formed are well-dispersed within the zeolite network, and leads to an increase of the adsorption properties, from 30 % to 60 % compared to the non-modified silver loaded zeolite. However, longer desilication times induce larger mesopores and consequently the formation of more larger Ag-nanoparticles. In this case, an important decrease of adsorption properties is obverved because of a lower adsorption specific surface on the Ag-nanoparticles, which demontrates the strong influence of the zeolite microstructure on the final Xe adsorption capacities.

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1053 - DEPENDENCY OF FRAMEWORKS AND CATIONS ON THE FUNCTIONALITY OF TRAPDOOR ZEOLITE

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Porous zeolites with thermal trapdoor behaviour are highly welcomed candidates in separating gases since the zeolites can present different internal cavity structures for different gases below the threshold temperature, such as N2 and CO2 [1]. However, the trapdoor frameworks as well as the “door-keeping” cations can affect the functionality of the trapdoor due to the differences in the crystal structure, porosity, and sorption behaviours [3-4]. The research estimated the influence of different metal ions (K+, Rb+ and Cs+) when connected to different frameworks (chabazite (CHA) and merlinoite (MER)) and compared the behaviours of the candidates under different conditions. All CHAs and MERs are successfully synthesised from the same parent Y-zeolite (Si: Al=2.3) under the same environment.

Gas molecules like H2 are prevented from entering the internal cavities till the thermal energy of the molecules is high enough to open the trapdoor while some molecules like CO2 can lower the energy barrier of the trapdoor cations, allowing them to pass the trapdoors in the eight-member rings (8MRs) into the internal pores. Moreover, the threshold temperatures vary from different trapdoor candidates to different gases. Unlike the CHA framework which can desorb the gas molecular smoothly, the adsorbed gas molecules in MER are more likely to be "locked" between the doors and become harder to desorb due to the perpendicularly orientated functional rings. That also led to a lower detectable Langmuir surface area (measured with CO2 at 273 K), but with a similar BET surface area (measured with N2 at 77 K). For the frameworks bounded with the same cations, the Langmuir surfaces detected in MERs are around 50% lower than that of CHAs.

The thermal behaviours of the trapdoor are further restricted by the bonded cations (K+ 1.52 Å, Rb+ 1.67 Å and Cs+ 1.81 Å) as the size and configuration of the cations resulted in structural differences in trapdoor blockage performance and thermal differences in thresholds temperatures in these in trapdoor systems. Based on the STA results (up to 500 °C), frameworks bounded with heavier (larger) cations are less likely to be hydrated resulting in around 3% higher mass left (95% weight left for CsMER, 92% weight left for RbMER and 89% weight left for KMER) after the experiment. The H2 sorption results also suggested the smaller (lighter) cations have lower threshold temperatures. An increase in around 0.14 Å cation radius leads to at least a 10 °C increase in critical temperature. Not only the thermal behaviour but the absorbability of H2 molecules are affected: the highest adsorption amount is achieved by Rb+ at above threshold temperatures.

The research compared the characterises and sorption behaviour of two different frameworks with various cations combined, showing the influence of cation size and framework structure on the trapdoor mechanism by analysing the dependency of the cation size and framework orientations on the trapdoor performance from crystalline, molecular, thermal and sorption behaviours.

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1065 - INFRARED SPECTROSCOPY FOR UNDERSTANDING OF EMERGING ZEOLITE CATALYSTS

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FTIR spectroscopy is a powerful characterization technique that provides important qualitative and quantitative information on the surface chemistry of zeolite catalysts. Herein, vibrational spectroscopy was applied to understand the synthesis-structure-performance relationships in recently emerged zeolite materials, including tetravalent element-substituted large-pore and hierarchical zeolites and a series of "isoreticular" zeolites with the same structure but variable micropore sizes.
The low strength of the Ge and Ti Lewis acid centers prevented their quantification based on the υ19b band of adsorbed pyridine (1445 – 1455 cm-1), an approach that is well accepted for aluminosilicate zeolites. On the contrary, the use of a well-resolved υ8a absorption band of pyridine (1608 cm-1) allowed us to distinguish weak Ti Lewis acid sites and silanol groups in conventional or layered TS-1. In turn, the measured integrated molar absorption coefficient enabled quantification of the acid sites in titanosilicate catalysts of different morphologies [1].
A spectroscopic study of germanosilicate zeolites showed a clear dependence of their acidic characteristics and related activity in glycerol ketalization on the pre-treatment conditions [2]. Exclusively Lewis acidity was detected in UTL germanosilicate, whereas the more active IWW catalyst was characterized by water-induced Brønsted acid centers, whose concentration increased with decreasing the activation temperature.
The location of acid sites in micropores of different sizes was validated in "isoreticular" aluminosilicate zeolites by FTIR-monitored co-adsorption of d3-acetonitrile and quinoline [3]. Furthermore, the matching of the experimental results to the predicted correlation of acid site location and apparent kinetics of ethanol-to-diethyl ether dehydration univocally confirmed the high potential of "isoreticular" zeolites as model catalytic materials to evaluate confinement-activity relationships in Brønsted acid-catalyzed reactions.

FTIR-monitored co-adsorption of alcohols in conventional and hierarchical aluminosilicate MFI zeolites evidenced the Riedel-Eley mechanism of the cross-etherification reaction that yields valuable cyclopentyl methyl ether [4-5]. In turn, the combined catalytic and FTIR spectroscopic studies clearly show that the selectivity of a zeolite towards the targeted asymmetric ether depends on the nature of dominating surface adducts (i.e., a neutral single H-bonded adduct; a bulky ionic H-bonded adduct; or a neutral cyclopentoxy group) whose fractions varied with the alcohol loading and the type of zeolite.
The power of FTIR spectroscopy to uncover important features of zeolite catalysts is expected to predestine further expansion of this method to examine emerging zeolite catalysts for rational design of their catalytic functions.

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1066 - MEASURING LOW AMOUNTS OF ADSORBATES CHALLENGES AND SOLUTIONS

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Not only the IUPAC recommends the use of argon at 87 K instead of nitrogen at 77 K for the characterization of porous materials[1], also the ISO 9277[2] describes problems when using the BET method for the determination by the use of the N2. So, regardless of the fact that N2 interaction problems with a material surface can influence pore volumes, specific area and pore size distribution results, N2 near 77 K is still the most common technique due to the availability of liquid nitrogen or for comparison reasons. However, this is only true for samples with a certain accessible pore volume under the appropriate measurement conditions. When it comes to samples with narrow ultramicropores or a very small surface area and almost no pore volume, such as thin films or non-porous samples N2 and also Ar reach their limits.

At cryogenic temperatures, both N2 (77 K) and Ar (87.3 K) can reach a saturation pressure of 101.3 kPa. However, if the surface area of the sample is very small and thus the number of adsorbed gas molecules on the sample is very little, only a minor change in the measured pressure of the sample gas is caused. With a reduction of the saturation pressure of adsorptives, the pressure range for BET and pore size calculations is reduced significantly, which results in a sensitivity enhancement of the sorption device. Another important difference to N2 at 77 K and Ar at 87 K is that normally the p0-values of the adsorptives are measured continuously during the measurements. If changing temperatures of liquid nitrogen or argon coolant during the measurements are assumed a p0 correction is necessary, which is not known for standard krypton measurements near 77 K. However, 3P instruments realized accurate temperature control, which prevents such errors.

In this way, we measured isotherms of small sample amounts at 78 K, 87 K, and more temperatures with krypton and other adsorptives such as nitrogen, argon, xenon, and carbon dioxide. Since both 78 K and 87 K are significantly below the triple point of krypton (Tcrit = 115 K), the gas already resublimates in the measuring cell at 0.28 kPa and 1.60 kPa respectively. However, within the pores a saturation pressure of 0.40 kPa and 3.07 kPa respectively of the undercooled liquid krypton phases is assumed, which enables the description of the measuring data and the study of temperature dependent adsorbate properties.

Our study demonstrates not only some inconsistencies regarding the cross sectional areas of adsorbate particles in the literature, but also gives recommendations for more consistent measurements and data reductions.

With new developed temperature control devices (cryoTune-series) one is able to control the temperature with less than 0.005 K deviation in a broad temperature range (78 K - 323 K). In order to show the influence of the measurement temperature on the adsorption result and the method-based evaluation respectively, mainly temperature dependent series of krypton isotherms were carried out at defined temperatures between 78 K and 120 K to characterize small sample amounts with noble gas atoms. The results of the study are expected to contribute to a better understanding of temperature-dependent adsorbate parameters and to promote the comparability of measurement results.

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1068 - INVESTIGATION OF CO2 ADSORPTION ON A SELECTION OF ZEOLITES BY IN SITU HIGH RESOLUTION POWDER X RAY DIFFRACTION ISOTHERM MODELING AND SIMULATION

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The adsorption of carbon dioxide (CO2) by porous materials such as zeolites is of great importance to address current environmental issues, and many zeolites have been developed as CO2 capture agents. Currently, combustion gases are identified as a major cause of the greenhouse effect. These gases are usually composed of a mixture of gases (N2, CO2, H2O, CH4 …), leading to competition for the most favorable adsorption sites and consequently a decrease in the zeolite's selectivity toward CO2 adsorption. Determination of the preferred sorption sites for each gas of the mixture is then necessary to gain insights into the host-guest and guest-guest interactions that govern the adsorption capacity of the adsorbent. We propose an approach where high-resolution powder X-ray diffraction and isotherm modeling and simulations are combined to determine the preferred sorption sites for pure CO2 and CO2 in a mixture and unravel the adsorption process of CO2 in a set of different zeolites.

The selected zeolites were chosen according to their affinity towards each of the constituents of the gas mixtures. We were especially interested in the silica-alumina ratio, so as to influence the hydrophobicity of the material, and also in the pore size to favor certain types of gas molecules, and this with the aim of increasing the adsorption capacity towards CO2. Monte-Carlo sorption simulations were conducted on each of the selected zeolites, in the presence of CO2 alone and CO2 in a gas mixture.

The evolution of the crystallographic structure of each zeolite with applied CO2 pressure, from 0 to 25 bar, was monitored in situ using high-resolution powder X-ray diffraction (ID22, ESRF). The specific positions of the CO2 molecules were extracted via Rietveld refinement, as well as the associated experimental adsorption isotherms. In addition to this overall information on the CO2 adsorption mechanism, local information, specific to each adsorption site, was also obtained from parametric Rietveld refinement [1], where structural evolution and adsorption modeling are intrinsically linked. Using such an approach on multiple CO2/zeolite systems, we showed that each adsorption site has its own adsorption mechanism following different adsorption models (Toth, Langmuir...). These experimental results, combined with Monte Carlo simulations, provide a deeper comprehension of the CO2 adsorption mechanisms, and also allow the homogeneity of the system to be observed through the host-guest and guest-guest interaction system specific to each zeolite.

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1082 - EXPERIMENTAL OBSERVATION OF ADSORPTIVE CAGE EFFECTS OF 1 ALKENES IN ALUMINIUM PAIRED CHABAZITE ZEOLITES

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In small-pore zeolites, such as chabazites (CHA), steric hindrance strongly affects the adsorption, diffusion and catalytic conversion of molecules. Molecules with a kinetic diameter close to that of the pore window of the zeolite (~3.8 Å), experience repulsive adsorbate-adsorbent interactions[1]–[3]. As a result of the close matching size, small-pore zeolites can differentiate between similar shaped and sized molecules. These small-pore zeolites have a wide variety of applications in chemical conversion processes, and in separative and purification processes of gas and liquid streams, such as methanol-to-olefins (MTO) conversion, selective catalytic reduction (SCR) of NOX, and air purification[4], [5]. However, a fundamental understanding of the relationship between the adsorption, diffusion and catalytic conversion of molecules in zeolite topologies is necessary as to optimize zeolites for potential separative or catalytic applications.

Generally, adsorption and diffusion properties of alkanes are monotonically chain length dependent[2]. However, for small-pore zeolites in which the pore system consists of cages connected through narrow windows, a non-monotonic chain-length dependence behavior is reported, and is often referred to as cage- and window effects[1], [2]. Here, increasing the chain length forces the molecule to coil up, or, once the chain-length becomes too long, protrude the pore window into the adjacent cage. This incommensurate fit between adsorbate and adsorbent lowers their adsorption strength and increases their diffusion rate throughout the zeolite. These effects are mostly experimentally or computationally studied using n-alkanes as probe molecules. Such fundamental adsorption effects have been speculated for other, more reactive, chemical groups as alkenes[3], yet have not been reported experimentally.

In our work, we investigated the adsorption properties at zero coverage of 1-alkenes on sodium-exchanged chabazite zeolites. Inverse gas chromatography (IGC) experiments with commercial and self-synthesized high-silica chabazite samples, with varying silica/alumina ratio (16-∞) were performed. We demonstrate that strong catalytic effects of Al containing chabazites, or too narrow pore windows of all silica chabazite can impede such experiments. Meanwhile, and as expected, the chemically similar n-alkanes did not react with these chabazite samples. Using recent developments in zeolites synthesis, a high silica chabazite with controlled alumina distribution was synthesized. In this zeolite, most of the Al-atoms are present as Al-pairs in the 6 membered ring (6MR) of the CHA framework. Using this aluminum paired chabazite limitations in alkene accessibility and catalytic effects were circumvented. With precise 1-alkene IGC measurements now possible, Henry constants, adsorption enthalpies, and entropies of 1-alkenes and n-alkanes up to C12 were determined. The results confirm and provide the first experimental proof of the existence of cage- and window effects of 1-alkenes on chabazite zeolites.

1098 - MWW SILICATES FROM THE 2D PRECURSORS TO THE 3D ACTIVE ZEOLITES

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Silicates, borosilicates and aluminosilicates MWW zeolites [1] consist of a layered structure in which two parallel non-interconnected 10 Member-Ring (MR) channel systems run one intra- and one inter-layer. 18.2 x 7.1 Å inter-layer supercages are formed upon the Organic Structure Directing Agents (OSDAs) removal and are connected by the inter-layer channel system. [2,3] The formation of the purely siliceous MWW zeolite requires two OSDAs: the hexamethyleneimine and the N,N,N-trymethyl-adamantammonium hydroxide. [2,3]

In this work, two MWW samples were hydrothermally synthesized using different synthesis gels (the Si-MWW_S and ITQ-1_S precursors samples respectively) and subjected to calcination in different atmosphere. The crystallinity, the structural order and the particle size distribution of both the as-synthesized and the calcined samples were determined by means of Powder X-Rays Diffraction (PXRD), 29Si Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR) spectroscopy and Scanning Electron Microscopy (SEM), respectively. The calcined samples were further characterized by N2 physisorption at 77 K to determine the Specific Surface Area and the porosity, and in-situ transmission infrared (IR) and 29Si{1H} Cross Polarization (CP) MAS-NMR spectroscopy to explore the nature of silanols. The organic structural directing agents (OSDAs) present inside the as-synthesized samples were studied using the elemental analysis of CHNS, 13C MAS-NMR and 13C{1H} CP-MAS-NMR. The degradation of the OSDA under calcination was studied by transmission IR Operando spectroscopy on the pelletized as-synthesized samples, coupled with a gas phase IR analyser.

The composition of the synthesis gel that undergoes hydrothermal treatment and the calcination procedures influence the properties of the synthesized MWW silicates. In particular, the composition of the synthesis gel influences the crystallinity and the structural imperfections of the materials obtained and determine the aggregation of the ITQ-1 crystals in form of empty macro-spheres of diameter comprised between 7 and 12 µm. Besides, the higher amount of OSDAs incorporated in the Si-MWW samples leads to lower defectivity and a significantly higher crystal growth along the c axes, compared with the ITQ-1 samples.

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1099 - NMR CRYSTALLOGRAPHY OF MONOVALENT CATIONS IN SILICON RICH ZEOLITES NA+ SITING AND THE LOCAL STRUCTURE OF NA+ SITES IN FERRIERITES

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One of the key features of silicon-rich zeolites (e.g. ZSM-5, ferrierite, mordenite, beta zeolite, …) is that they exhibit a medium or high number of crystallographically distinguishable framework T sites occupied by either exclusively Si or by both Al and Si atoms. This feature, together with a low Al content, leads to a variability of the Al siting in the framework. Since the positively charged catalytically active species (protons, metal cations, and metal-oxo species) bind to the AlO4- tetrahedra to balance their negative charge, the positions of Al in zeolite frameworks control the location of the active sites, which in turn affects the catalytic activity and selectivity. The determination of the positions of monovalent cations for each distinguishable T site occupied by Al (i.e., the siting of monovalent cations) is essential to evaluate the catalytic and sorption properties of cation exchanged silicon-rich zeolites. High and ultra high-resolution 23Na (MQ) MAS NMR spectroscopy (500 and 900 MHz spectrometers) of dehydrated Na(I) exchanged zeolites was employed to monitor Na(I) ions in three silicon-rich ferrierte samples with different Al siting.[1,2] Periodic DFT calculations including extensive molecular dynamics conformational sampling of all possible Na(I) sites for all the possible distinguishable Al(T) sites were performed employing the cp2k program. The B3LYP 23Na NMR shielding values were evaluated utilizing the Gaussian program and seven coordination shell clusters. We reveal the siting of Na(I) balancing framework Al atoms located in all the distinguishable framework T sites of ferrierite. It was found that Na(I) ions can occupy several cationic sites formed by one type of framework Al atom and that on contrary to the 7Li(I) ions, 23Na NMR shielding reflects predominantly geommetry of the Na(I) site – size of the ring accommodating the Na(I) ion.

Concluding, although the ultra high-resolution 23Na (MQ) MAS NMR spectroscopy represents a powerfull tool to analyze Na(I) ion siting in the complex matrix of silicon rich zeolites, a multispectroscopic approach combining 27Al, 23Na and 7Li (MQ) MAS NMR spectroscopy can be recommended for the analysis of the siting of monovalent extra-framework cations in silicon rich zeolite matrices as well as for the analysis of the siting of framework Al atoms in complex matrices of silicon rich zeolites.[3]

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1108 - UNDERSTANDING THE EVOLUTION OF MICROPOROSITY DURING HIERARCHIZATION TREATMENTS OF ZEOLITES CONTAINING SIDE POCKETS

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Zeolites are materials widely used in industrial catalytic applications. The diffusion of molecules, which sizes approach that of the micropores can be strongly hindered by the narrow pore system. This, together with the often extended diffusion path length, impacts negatively the catalytic efficiency of a given process. Zeolite hierarchization allows for creating secondary porosity in the mesopore range, interconnected to the microporous system, diminishing the diffusion path lengths and allowing for maximizing effectiveness factors in catalysis.

In an ideal zeolite hierarchization process, solely intracrystalline mesopores are generated whilst micropore volume remains preserved. Many hierarchization methods have been disclosed to create secondary porosity in zeolites, and their impact on the development of mesopores has been widely described in the literature1. Yet, diligent characterization of the evolution of the microporous texture is generally neglected. Indeed, the impact of such post-synthetic modifications on the distribution and accessibility of micropores is only scarcely highlighted2-3-4. Textural properties of micropores are yet a crucial parameter when it comes to understand the catalytic performance of zeolitic materials. In a recent study, we demonstrated that hierarchization strongly impacts the micropore distribution of MCM-22 zeolites5.

In this communication, we firstly present the impact of hierarchization treatments on the evolution of the micropore system of zeolites featuring pseudo-one dimensional porosity with side pockets. A set of hierarchical MOR and EUO structured modified zeolites by different hierarchization treatments (steaming, acid leaching, ammonium fluoride etching) was prepared. The adsorption of probe molecules with different kinetic diameters (N2, Ar, n-nonane, n-hexane, toluene, 2.3-DMB) was investigated on these samples with the aim to understand the evolution of the microporous system.

It was found that hierarchization treatments generally lead to a slight decrease of the micropore volume determined by N2 or Ar physisorption. For the MOR structured zeolites, the bimodal size distribution (side pockets and main channels) was importantly impacted as a function of the applied post-synthetic treatment. Steaming treatments destroy preferentially the side pockets, whereas acid leaching was found to have a stronger impact on the main channels. Ammonium fluoride etching allows for majorly preserving main channels compared to acid leaching but has a stronger impact on the amount and distribution of side pockets. The destruction of the side pockets in MOR zeolites leads to two consequences: (i) the enlargement of the microporosity and (ii) the achievement of a bi-dimensional porous network allowing for the diffusion of organic molecules. The decrease of micropore accessibility for organic molecules upon severe hierarchization treatments probably due to localized framework collapse was further observed.

The enlarged microporosity index (phi Ar) could be deduced from argon physisorption isotherms measured on n-nonane preadsorbed samples. A (phi Ar value of 0 corresponds to samples for which n-nonane molecules are hardly confined and block the access to micropores for Ar molecules. The value 1 is reached for samples with enlarged microporosity, for which the micropore size no longer allows for the confinement of n-nonane molecules. This has been confirmed by organic vapour physisorption.

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1112 - CONFINED WATER CLUSTER FORMATION IN WATER HARVESTING BY METAL ORGANIC FRAMEWORKS CAU 10 H VERSUS CAU 10 CH3

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Several metal-organic frameworks excel in harvesting water from the air or as heat pumps as they show a steep increase water uptake at 10-30 RH%.[1] The key to achieving favourable water isotherms seems to be an alternation of moderately hydrophilic (e.g. framework hydroxyls) and hydrophobic sites (e.g. phenylenes) within mere nanometres. But even among MOFs that display this alternation, the sought after sudden steep water uptake in the 0.1 -0.3 p/p0 range is rare. Herein we studied CAU-10-H and CAU-10-CH3 with –H, -CH3 corresponding to the functions grafted to the organic linker. CAU-10-H shows a steep water uptake around 18 RH% making it interesting for water harvesting.[2] Yet the subtle replacement of -H by -CH3 in the organic linker drastically changes the water adsorption behaviour to water uptake at much higher humidity values, that is also less steep. We unravelled the materials' structural deformation and water ordering during adsorption with in situ sum-frequency generation, in situ second-harmonic generation, in situ X-ray diffraction, and molecular simulations. In CAU-10-H an energetically favourable polar water cluster, identified via single crystal XRD, is formed in the hydrophobic pore, tethered via H-bonds to the framework Al-OH groups. In the (H2O)14 cluster on average 3.3 hydrogen bonds can be formed per water molecule. In contrast, in CAU-10-CH3 such a favourable cluster cannot form. The steric hindrance of the –CH3 groups lowers the number of average hydrogen bonds to 2.3, which is energetically less favourable. Indeed, computationally we found that the energy difference of H2O within the cluster in CAU-10-H with respect to free water is about -9.2 kcal/(mol H2O), while in CAU-10-CH3 it's only -7.7 kcal/(mol H2O). With in situ X-ray diffraction and in situ sum-frequency generation at different relative humidity values we studied the abrupt (first order) phase transition of CAU-10-H and the more gradual phase transition of CAU-10-CH3 upon water adsorption of a centrosymmetric structure to a polar structure, including polarly organised water.

Moreover, by relating our findings to the features of water adsorption isotherms of a series of MOFs we conclude that favorable water adsorption occurs when sites of intermediate hydrophilicity are present in an otherwise hydrophobic structure, and, very importantly, the geometry of the pore and positioning of these hydrophilic sites allow for the formation of an energetically favorable water cluster. We believe that this conceptual understanding of the mechanism leading to the desired water adsorption properties can aid in "de novo" design of water harvesting materials.

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1123 - STRENGTH OF ZR LEWIS ACID SITES DECIDES ON TERPENE REDUCTION SELECTIVITY

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Meerwein-Ponndorf-Verley (MPV) reduction is a hydrogen transfer reaction enabling chemoselective formation of alcohols from corresponding aldehydes and ketones under mild conditions. The reaction is, i.a., tolerant to other easily reducible groups such as -NO2 and C=C double bond. Sn-, Zr-, and Hf- substituted Lewis acid zeolites are established heterogeneous catalysts for this reaction. Sn-zeolites are more active in MPV reduction of ketones, while Hf- and Zr-silicates exhibit a higher activity for MPV reduction of aldehydes. In addition, different types of the Lewis sites ("open" M(SiO)3OH vs. "closed" M(SiO)4, where M=Sn, Zr, Hf) differ in the catalytic properties. Sn "open" sites were proved to catalyse, i.a., sugar isomerization (which is principally an intramolecular MPV reaction), while the Sn "closed" sites catalyse, e.g., dehydration reactions [1]. However, for Zr sites such ascription of the catalytic activity is missing. Moreover, the MPV reaction selectivity decreases if the reaction system allows also other simple hydrogen transfer reactions such as intramolecular enal reactions. This is the case of terpenes like citronellal, which forms isopulegol isomers besides the citronellol under the MPV reaction conditions with 2-propanol as hydrogen donor.

In this contribution, we thoroughly characterized the Lewis acid sites in Zr substituted MFI and beta zeolites. We found a correlation between the reaction selectivity in the citronellal MPV reduction with 2-propanol and type of the acid sites present in the catalysts. Two samples of Zr-beta with different acidic properties (one rich in the "open" sites, the other rich in the "closed" sites), conventional Zr-MFI and silica-metal oxide pillared Zr-MFI-pill [2], together with a Sn-beta reference, were analyzed by adsorption of deuterated acetonitrile (d3-ACN) and acetone probe molecules followed by FT-IR spectroscopy. The d3-acetonitrile probes the "open" Zr sites but it does not interact with the "closed sites" [3]. In contrast, the acetone probes both "open" and "closed sites" [4]. In the catalytic tests, the Zr-MFI and Zr-MFI-pill samples provided only isopulegol (yield 7% and 33%, respectively, after 6 h at 70°C) while the Zr-beta rich in the "open" sites gave 17% yield of citronellol and 77% yield of isopulegol and the reaction over Zr-beta rich in the "closed" sites yielded 64% of citronellol and 15% of isopulegol. Sn-beta gave 70% of isopulegol and 3% of citronellol under the same conditions.

Linking the data from the acidity analysis, we conclude the citronellal MPV reduction to citronellol occurs over the "closed" sites, while the intramolecular enal reaction to isopulegol is catalyzed by the "open" sites. Zero yield of citronellol over the Zr-MFI catalysts can be explained by the fact the "closed" sites are likely present inside the micropores, which are too narrow to accommodate bimolecular MPV reaction transition state.

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1133 - SOLID STATE NMR SPECTROSCOPIC INVESTIGATION OF SUPPORTED FLUORINATED IONIC LIQUIDS FOR INTERFACE ENHANCED SUPPORTED IONIC LIQUID PHASE CATALYSTS

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Supported Ionic Liquid Phase (SILP) catalysts stand out as a promising class of materials with remarkable advantages in homogeneous catalysis due to their straightforward separation from the reaction media and reuse of the metal complex [1]. For preparing these solids, a mixture of an ionic liquid (IL) and a molecular catalyst is impregnated onto a solid porous support. The catalytic properties of the active sites will depend not only on the individual properties of the support, metal complex, and ionic liquid but also on their interactions [2]. Therefore, a microscopic comprehension of the IL film behaviour and interaction with the support inside a porous material is vital to develop SILPs potential. This will guide the design of task-specific ILs whose moieties aim to enhance the interaction with the support and assist the molecular catalyst localization, at either the gas/liquid or the liquid/solid interface, tuning its performance in the selected catalytic application.

Solid-state NMR spectroscopy under Magic Angle Spinning (MAS NMR) is a powerful technique to study the structure and dynamics of both solid and liquid phases inside a porous material on a molecular level. Here, we investigated the interaction of novel imidazolium-based task-specific ionic liquids with a silica surface; our incorporation of a fluorinated aryl moiety aimed at the self-assembly of the IL molecules and an orientation perpendicular to the support. By combining one and two-dimensional NMR techniques, we proved the existence of this targeted interaction, characterized some aspects of the molecule conformation over the support, and asses their potential as ligands for interface-enhanced SILP catalysts.

Four task-specific alkyl aryl fluorinated ILs were deposited onto 29Si-enriched ordered mesoporous silica SBA-15. 19F NMR spectra of the obtained SILP materials exhibited chemical shift changes compared to the parent IL. New peaks, line broadening, and shorter longitudinal relaxation times (T1) suggest a different chemical environment due to the interaction of the IL with the silica surface. 19F {29Si} Cross Polarization (CP MAS) not only proved the proximity of the fluorinated moiety to the silica surface but also indicated the predominant magnetization transfer to silicon atoms involved in siloxane bridges (Q4) and single silanol (Q3) sites. The two-dimensional method 1H-19F HETCOR supported this observation. REDOR experiments allowed us to determine the internuclear distance of the interacting spin pair, 29Si and 19F; according to the results, the two identified chemical environments present distances in the range of 2.0 to 2.9 Å and different mobility behaviour, depending on the impregnated IL. Finally, through 1H-29Si HETCOR and 1H-1H DQMAS, we evidenced the interaction of the alkyl or poly(ethylene glycol) moiety with the silica, their conformations, and its possible effect on the molecule configuration over the surface. Overall, the NMR data provided evidence that allowed us to propose a tentative surface configuration model, proving the effect of the fluorine moiety insertion as a director for the molecule self-assembly over a silica surface.

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1170 - INVESTIGATION OF THE NATURE AND STABILITY OF ALUMINUM SITES IN ZEO 1 VIA IN SITU INFRA RED SPECTROSCOPY AND SOLID STATE NMR

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Extra-large pore zeolites are highly desirable materials for several industries, including heavy fossil oil conversion and biomass upgrading [1]. Despite the successful synthesis of several stable extra-large pore zeolites (UTD-1, EMM-23, etc.), these materials are obtained as pure silicates, boro-silicates, or aluminosilicates with Si/Al > 50, thus requiring post-synthetic modification to insert or enrich the aluminum content for catalytic applications [2]. ZEO-1 is a recently reported stable extra-large pore aluminosilicate zeolite that features a three-dimensional framework with three super cages formed by the interconnection of 16+16, 16+12, and 16+12 channels. Furthermore, ZEO-1 is a strongly promising catalyst since it can be synthesized directly with a relatively low Si/Al = 15 compared to its counterparts [3]. In this study, we provide a comprehensive investigation into the nature and stability of the Al sites of ZEO-1. Our results show that ZEO-1 possesses two different chemical environments for Al coordination within its framework. Figure 1 shows the 27Al NMR spectrum of ZEO-1 before and after calcination. All the Al species in ZEO-1 before calcination are tetrahedrally coordinated, as confirmed by the broad peak composed of two shoulders corresponding to a chemical shift around 56 ppm. Upon calcination, the spectrum changes remarkably, and octahedral extra-framework Al species formation is evident by the peak at around 0 ppm. As for the Bronsted acid sites, it is possible to distinguish a band at 3640 cm-1 and a broad and weaker band appearing along silanol nests between 3600-3500 cm-1. We intend to remove the OSDA by a benign method to investigate whether the dealumination is due to structural stress or a consequence of the strong interaction with the phosphonium OSDA. Moreover, a variety of infrared probe molecules will be used to assess the nature, strength, and accessibility of Bronsted and Lewis acid sites.

Figure 1 27Al MAS NMR spectrum of ZEO-1 before and after calcination.

Figure 2. FTIR spectra in the OH region of ZEO-1 after calcination.

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1184 - HOST GUEST MFI ASSEMBLIES CORRELATED DISORDER AND PHASE TRANSITION INHIBITION BY A SMALL GUEST MODIFICATION

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The unique pore geometries and structures of zeolites, widely exploited in industry, allow also to form host-guest functional materials containing molecules and polymers for drug delivery, optical and electronic applications to name a few. Following our researches on the interactions between organic structure directing agent (OSDA) and zeolite frameworks, we recently investigated the nanoscale disorder in prototypical host-guest assemblies, made of silicalite-1 (host) and OSDA (guest) [1]. Notably, we examined in great detail the modifications induced by changing the most efficient OSDA tetrapropylammonium (TPA) by the very similar tripropylethylammonium (TPEA) using for both OSDAs a fluoride route that usually insures a high degree of local order. Long- and short-range organization and ordering were characterized by complementary XRD, Raman and multinuclear NMR (13C, 14N, 29Si) at ambient and variable low temperature. An in-depth structural study was carried out by x-ray structure determination and 2D NMR 29Si-29Si INADEQUATE correlations, including an up-to-date analysis of anisotropic atomic displacement parameters and a new fitting approach to estimate correlated disorder from NMR.

The results allow to demonstrate how the positioning of the less symmetric TPEA guest in the MFI host framework leads to a correlated geometrical disorder for half of the Si sites. From 13C NMR, XRD and DFT calculations, we confirmed that ethyl arms are preferentially located in the straight channels of the MFI framework along the b axis, in agreement with a previous study [2]. In these channels, the ethyl arms can adopt one of the two possible directions leading to a positional disorder, and to related host deformations and mechanical stress. We have noticed that half of the [SiO4] tetrahedra in the MFI framework are forming a columnar arrangement along the b axis. Such an arrangement does not allow the relaxation of the mechanical stress induced by the presence of ethyl arms. This is the probable origin of the correlated disorder between Si units observed on the 2D NMR 29Si-29Si correlations. Further, this correlated disorder blocks the collective atomic displacement necessary to the monoclinic-orthorhombic phase transition to occur, leading to a locally disordered structure (NMR, Raman) and to the inhibition of the transition as observed when replacing TPA by TPEA.

This is the first time that such a drastic effect of a small guest's modification (TPA → TPEA) on a zeolite phase transition is evidenced and explained by the presence of correlated disorder. This novel result might be extended to other systems opening new perspectives in the design of materials with tuned properties through the control and exploitation of correlated disorder.

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1191 - REVEALING THE AMORPHOUS TO CRYSTALLINE TRANSFORMATION IN ZEOLITE SYNTHESIS USING IN SITU HIGH ENERGY X RAY TOTAL SCATTERING MEASUREMENT

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Deep understanding of the amorphous-to-crystalline transformation at the sub-nanometer scale involved in the synthesis of zeolites, especially in the early stage where amorphous solids are the dominant component, is still insufficient, due to the lack of effective characterization techniques to identify the amorphous structures. Pair distribution function (PDF) analysis, by which different interatomic distances can be derived from total scattering data, is an alternative approach to give insights into the structures of materials covering short-to-medium atomic arrangement, and therefore is particularly useful to analyse the architecture of liquids, glasses and other amorphous materials. The PDF analysis based on high-energy X-ray total scattering (HEXTS) technique using synchrotron X-ray, featuring improved real space resolution, has been tentatively applied to the researches on the structural changes in the zeolite precursors [1]. Recently, in situ HEXTS-PDF analysis has also been developed, which is expected to be a promising approach to track the structural evolution of amorphous precursors towards crystalline zeolites under the practical hydrothermal conditions [2]. Herein, we performed in situ HEXTS-PDF analysis, combined with other characterization techniques, to explore the crystallization scheme of SSZ-13 zeolite, and the evolution of the local ring structures in the amorphous precursors during the synthesis was observed for the first time [3].

SSZ-13 zeolite was synthesized at 160 °C either in a conventional Teflon-lined stainless-steel autoclave under rotation, or in a homemade hydrothermal reactor system. The in situ HEXTS measurements were carried out on the BL08W high-energy X-ray diffraction beamline ($\lambda = 0.1076$ Å) at SPring-8. The obtained scattering data were processed to obtain the reduced PDF, $G(r)$. The relative PDF analysis, $\Delta G(r)$, was also conducted by subtracting the reference scattering data [2].

In situ HEXTS-PDF analysis is conducted during the synthesis of SSZ-13 zeolite to investigate the structural changes of the amorphous aluminosilicates while preserving their “real state”. Since the synthetic system contains a mixture of water, dissolved reactants, amorphous aluminosilicate solids and later newly-formed crystalline zeolites, all of which can result in X-ray scatterings, the differences among the total PDF patterns throughout the whole synthesis time can hardly be identified. Therefore, the relative PDF analysis is further carried out. The scattering profile of the initial state (the moment that the synthetic system reached set temperature) is used as a reference and subtracted, and consequently only the subsequent structural changes will be reflected. It is demonstrated that ordered 4Rs, rather than cha cage consisting of 6R and 8R, are dominantly formed in the early stage. These existing ordered 4Rs subsequently contribute to the formation of d6r and cha composite building units with the assistance of organic structure-directing agent to construct embryonic SSZ-13 zeolite crystallites, which further trigger the crystal growth. Such ring structure evolution during the synthesis can hardly be detected by other conventional ex situ characterization techniques.

1227 - IN SITU INVESTIGATION OF WATER HARVESTING BY CAU 10 X (X= OH CH3) METAL ORGANIC FRAMEWORKS A 2 STEPS PROCESS

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Many metal organic frameworks (MOFs) exhibits interesting harvesting water capabilities from the air or as heat pumps as they demonstrate a steep increase in water uptake in the range 10-30 RH% [1]. Optimal water isotherms are represented by an alternation of moderately hydrophilic and hydrophobic sites. However even within the MOFs exhibiting such alternation, the required steep uptake of water relevant for real applications is quite scarcely met [2]. Recently, we have studied the CAU-10-X (X=H, CH3) members and unravelled the materials' structural deformation and water ordering during adsorption with in situ sum-frequency generation, in situ second-harmonic generation, in situ X-ray diffraction, and molecular simulations [3]. We have shown that the steric hindrance of the -CH3 group lowers the number of average hydrogen bonds from 3.3 to 2.3 explaining the difference in the water uptake behavior. Those data have shown that CAU-10-H undergoes a strong first order phase transition while CAU-10-CH3 exhibits a more gradual phase transition between a centrosymmetric structure to a polar structure.

Among the various members of the CAU-10-X family, the composition X=OH is particularly interesting as this is the only composition where a steep-2 steps process is taking place within the isotherm [2]. On the contrary, the composition X=CH3 is quite representative of several members and exhibits a gradual phase transition. Aiming to determine a conceptual understanding of the mechanism resulting from this water absorption to design “de novo” water harvesting materials, we have investigated the members X=OH and CH3 using in-situ relative humidity powder diffraction. We present in Fig. 1 our results for X = OH. These results demonstrate the existence of an intermediate phase which has not been observed before. Similar results were obtained for X=CH3 and the effect of temperature is stabilizing this intermediate phase.

The existence of this intermediate phase stabilized under temperature and moderate relative humidity shed some new light in our understanding of this mechanism and call for further investigation of the water uptake mechanism. Contrary to previously believed results, it is demonstrating the uniqueness of the behavior CAU-10-H against all other members of the family. This is effectively suggesting that irrespective of the functional group besides X = H, the associated steric hindrance always leads to a 2-step process with phase coexistence explaining the previously reported gradual changes in the isotherms. Extending our conclusions to the general case of MOFs, this is suggesting that MOFs exhibiting a gradual adsorption isotherm are possibility hiding multiple phases.

1234 - COMPREHENSIVE UNDERSTANDING OF BASE CATALYSIS DERIVED FROM N SPECIES IN SILICA AND CARBON FRAMEWORKS

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Base catalysts demonstrating good activity for C–C bond-formation reactions are widely used in various industries to synthesize fine chemicals, cosmetics, pharmaceuticals, and fragrances, among others. A number of base catalysts have been studied and reported. Environment-friendly heterogeneous catalytic systems have gained considerable attention owing to the advantages associated with the separability and recyclability of the corresponding catalysts compared with homogeneous catalytic systems. Compared with the well-studied amine-functionalized silica, nitrided silica and carbon nitride have not yet been explored in detail. Based on the available research, these materials may potentially serve as solid base catalysts with high activity.

Nitrided mesoporous silica is synthesized by reacting mesoporous silica with ammonia at temperatures of 773–1423 K[1-9]. Oxygen atoms in the silica framework are substituted by nitrogen atoms, and the basicity of the catalyst arises from the presence of a lone pair on the framework nitrogen atom. The base-catalytic performance of nitrided mesoporous silica depends on the type of nitrogen species. For instance, the catalytic activity of this type of materials for aldol and Knoevenagel condensation shows the order primary amine > secondary amine ≈ tertiary amine[6]. Moreover, we previously developed a new class of base catalysts based on nitrided silica; further functionalization, such as by methylation[2], of the nitrogen site enhanced the basicity of the nitrided mesoporous silica, and the resultant catalysts successfully catalyzed the Knoevenagel condensation of a high-pKa reactant (diethyl malonate)[2,3] and the CO2 addition reaction[5,7]. Carbon nitride has also been studied as a potential solid base catalyst. Porous carbon nitride (PCN) shows higher catalytic activity compared with dense carbon nitride owing to the high mass diffusion originating from its large surface area and nanosized pores[9]. Amine-functionalized silica materials have been widely studied as solid base catalysts[10].

In this study, we compared the basicity and catalytic activity of nitrided mesoporous silica SBA-15 with those of PCN and a series of SBA-15 materials functionalized with four different types of amines. We selected the Knoevenagel condensation reaction and performed studies on the adsorption of acidic molecules to evaluate the basicity of catalysts. Specifically, the base catalytic properties of the materials were evaluated by the Knoevenagel condensation of benzaldehyde with active methylene compounds. The adsorption of acidic molecules like CO2, benzoic acid, and phenol is commonly used as a typical tool to evaluate catalyst basicity. Because CO2 molecules are smaller than the substrates used in the catalytic reactions, the basicity of the sample can be evaluated without the influence of steric hindrance; thus, the basicity of the catalysts was evaluated by CO2-probe FT-IR spectroscopy at ambient temperature. By comparing the CO2-probe FT-IR spectra with those of the catalytic reactions, we can obtain a comprehensive understanding of base catalysis based on the nitrogen species inside the silica framework.

1247 - INTERACTION OF ETHENE WITH SILVER ON SMALL PORE AG ZEOLITES

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Many chemicals and polymers rely on ethylene as building block and for this reason, its production exceed the 200 million tons per year [1]. Ethene is mainly obtained by steam cracking of naphtha and is accompanied by many other hydrocarbons being ethane the most abundant. The separation required for their use is performed by cryogenic distillation, which is one of the most energy demanding processes in chemical industry and then, there is a need in developing a low energy demanding process [2]. One of the most promising approaches is the use of zeolites which have shown unique selectivity for ethene/ethane separations at ambient temperature dramatically reducing the energy consumption for such process [3]. The adsorption selectivity can be enhanced by incorporating metal cations such as Ag+ in zeolites which interacts with the double bond of ethylene [4]. Depending on the pre-treatment of the Ag-zeolite and the framework topology different species including atomically dispersed cations, metal clusters or nanoparticles can be formed. The aim of this work is to investigate the influence of the zeolite structure on the silver species formed and their interaction with ethylene by using a series of spectroscopic techniques such as UV-Vis, ss-NMR, Inelastic Neutron Scatering (INS) in combination with DFT calculations.

Three small pore zeolites of CHA, RHO and LTA type with similar Si/Al ratio Si/Al $\approx$ 5 and with silver contents Ag/Al $\approx$ 0.6 for the AgCHA, AgRHO and Ag/Al $\approx$ 0.3 for AgLTA have been prepared by chemical exchange. After evacuation at 400 ºC, the UV-Vis spectra show that Ag+ are dominant in AgRHO, Ag+ and mainly Ag3+ clusters are present in the AgCHA and metal nanoparticles in the AgLTA. The 109Ag NMR spectra allows the observation of signals about 20-60 ppm of Ag+ in the hydrated samples, whereas after evacuation, cationic silver appears at higher field and new signals of Ag0 at around 5260 ppm grow. The intensity of the signals depends on the zeolite sample. Subsequent adsorption of 13C2H4 shift all 109Ag NMR signals to lower field proving the interaction with ethylene and the corresponding 13C NMR signal are shifted to high field compared with the gas phase. Moreover, the δ13C of adsorbed ethylene depends on zeolite structure and thus the silver species present and on the ethylene loading. The experimental INS spectrum of ethylene adsorbed on the Ag-CHA sample was measured and simulated by DFT methods considering Ag+ and Ag3+ sites. In both cases the results are compatible with the experimental results, although the interaction is stronger with Ag+.

Summarizing, the combination of a series of spectroscopic techniques with DFT theoretical calculations allows to propose a model for the adsorption of ethene on silver in small pore Ag-zeolites.

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1330 - ADVANCED ELECTRON MICROSCOPY FOR THE INVESTIGATION OF FAU Y THERMAL DEALUMINATION – STRUCTURAL PATTERNING REVEALED

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Y-Faujasites are a keystone for heterogeneous catalysis as an irreplaceable asset for carbon chain cracking reactions thanks to their tuneable acidity and wide microporous channels. These two very specific features make FAU-Y a central player as an active hydrocracking catalyst in crude oil refining, upgrading of biologically sourced oils and plastics recycling. However, the optimization of both acidic and textural properties for its different applications requires post-synthesis processing steps promoting the dealumination or desilication of initially pristine sub-micron sized crystals. These steps usually employ thermal treatments in the presence of water vapor, classically referred to as “steaming”, and chemical reagents such as inorganic and organic acids. The mechanisms leading to stabilized crystals with adequate acidity and textural properties have been evidenced to a certain extent by various approaches including quantum calculation, 1H and 27Al nuclear magnetic resonance (NMR), X-ray absorption spectroscopy (XAS), N2-physisorption, mercury porosimetry and electron microscopy. Recent reports have underlined the role of defects in the initial crystal structure for promoting structural dealumination[1] on FAU-Y and for patterning the mesoporosity on MFI[2] and on MOR[3]. The role of twins in the structure for guiding the formation of mesopores was also shown some time ago by electron microscopy for FAU-Y[4].

The systematic relationship between structural defects and dealumination features in FAU-Y however remains to be established on a multiple criteria basis, which is complicated by the fact that defects are expressed with an important heterogeneity in a population of crystals. Thus, bulk characterisation methods may only provide an averaged comprehension of the role of defects on the amplitude of the effects of dealumination, typically on acidity and mesoporosity. To provide a phenomenological description of the role of defects in dealumination, one must provide spatially, chemically, and structurally resolved information in the defective environment of the crystal. This is made possible by the electron microscope.

Here, we provide new electron microscopy data of variably dealuminated FAU-Y crystals for which different quantitative information are extracted. First, detailed single crystal STEM-EDXS maps were acquired on 70 nm thick ultramicrotomy sections. Local crystal-surface STEM-EELS data were acquired at the Al and Si L-edges to describe the nanometer scale relationship between Si/Al ratios and mesopore/surface morphology. Last, single-crystal electron tomography data and high-resolution secondary electron SEM data are employed to build a topological description of the mesoporous network at the surface and inside the crystals. The different data are associated to specific orientations in the crystal structure of the FAU-Y derived from BF HR-STEM images. Compared with bulk FX elemental analysis, XRD and N2-physisorption data; we propose a mesoscale model for describing the role of structural defects in the dealumination of FAU-Y zeolites.

1332 - INSIGHT INTO THE INTERDEPENDENCE OF NI AND AL IN BIFUNCTIONAL NI ZSM 5 CATALYSTS BY NI K EDGE XAS ANALYSIS

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Catalyst design is crucial for improving catalytic activity and product selectivity. In a bifunctional Ni/ZSM-5 zeolite type catalyst, catalytic properties are usually tuned via varying Al and Ni contents [1]. While changes in acid properties associated with Al sites are usually closely investigated, Ni phases, however, receive inadequate attention. Herein, we present a systematic structural study of Ni in the Ni/ZSM-5 materials by Ni K-edge XANES (X-ray absorption near edge structure) and EXAFS (extended X-ray absorption fine structure) analyses, to monitor the local structure and chemical state of Ni species in the catalysts. In combination with XRD and TEM we resolved the changes in the local environment of Ni species induced by the different Al contents of the parent ZSM-5 prepared by a “green”, template free technique[2].

Ni species in Ni/ZSM-5 exist as NiO crystals (3–50 nm) and as charge compensating Ni2+ cations. The Ni K-edge XANES and EXAFS results enabled the quantification of Ni-containing species. At a low Al to Si ratio ($n_{Al}/n_{Si} < 0.04$), the NiO nanoparticles predominate in the samples and account for over 65% of Ni phases. However, NiO is outnumbered by Ni2+ cations attached to the zeolite framework in ZSM-5 with a high Al to Si ratio ($n_{Al}/n_{Si} = 0.05$) due to a higher number of framework negative charges imparted by Al. The obtained results show that the number of highly reducible and active NiO crystals is strongly correlated with the framework Al sites present in ZSM-5 zeolites, which depend greatly on the synthesis conditions. Therefore, this kind of study is beneficial for any further investigation of the catalytic activities of Ni/ZSM-5 and other metal-modified bifunctional catalysts.

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1206 - SCANNING TRANSMISSION ELECTRON MICROSCOPY FOR STRUCTURE ELUCIDATION OF LOW DIMENSIONAL ZEOLITIC MATERIALS

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Zeolites have been used widely in industry as size- and shape-selective catalysts and adsorbents, because of their ordered microporous structure of molecular dimensions. The number of topologically different zeolites today exceeds 250, each with a unique pore size, shape and channel dimension. Most zeolites have 3-dimensional (3D) periodic structures, some materials have been possible to grow into 2-dimensional sheet like morphologies that are periodic in two dimensions.

Over the last decades methods for 3-dimensional electron diffraction (3D ED) have opened up a more accessible route for structure determination from sub-micrometer-sized crystals. Structure determination of low dimensional materials however still remains a challenge. The lack of 3D periodicity of the reciprocal lattice limit the possibilities to retrieve a 3D structure ab-initio from the diffraction data.

Recent developments in modern electron microscopes are now enabling several opportunities for real-space imaging of porous solids. The aberration correction makes it possible to obtain scanning transmission electron microscopy (STEM) images of sub-Ångström resolution. The recently developed integrated differential phase contrast (iDPC) technique opens up for imaging with electron beam doses an order of magnitude lower than before.

Two examples of low-dimensional zeolitic materials are the layered PST-9 and the zeolite nanotubes. PST-9 was found as an intrinsically layered material found as an intermediate in the synthesis of EU-12. Using aberration-corrected STEM imaging images of single sheets with a thickness of <2 nm it was possible to obtain images of atomic resolution. Based on the STEM images and the periodicities revealed by the 3D ED data an atomic model for the structure of the layered PST-9 was obtained.

Recently we have shown for the first time a 1-dimensional tubular zeolitic material combining meso- and microporosity. High-resolution annular dark-field scanning transmission electron microscopy (ADF-STEM) and integrated differential phase contrast (iDPC) images were obtained both perpendicular to and along the nanotube direction after sectioning the nanotubes by ultramicrotomy. Ten identical repeating units with square-like features are frequently observed around the circumference of the nanotubes, and the distance between the adjacent units is about 12-13 Å. Images acquired perpendicular to the nanotube direction reveal the microporous nature of the projected wall structure in more detail. Based on the structures observed in the iDPC STEM images and the periodicity along the tube direction obtained by 3D ED, the structural model of the nanotube can be deduced. The structure imposes a curvature of this atomically thin zeolitic sheet into a nanotube.

SHORT ORAL - POSTER ABSTRACTS

CATEGORY: ADVANCED SYNTHESIS (ZEOLITES, ZEOLITE-LIKE MATERIALS, MOFS, OTHER POROUS SOLIDS)

1035 - DIRECT INTERZEOLITE TRASFORMATION OF BOROSILICATE MWW TO METALLOSILICATE BEA TYPE ZEOLITES AND THEIR APPLICATION AS LEWIS ACID CATALYSTS

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Metallosilicate has been suggested as promising catalyst in biomass conversion, selective oxidation, etc., owing to its stable metal species embedded in the zeolitic structure and its unique acidic properties [1]. To develop high-performing metallosilicates, the interzeolite transformation, i.e., the transformation of parent zeolitic material into the new zeolitic material, have been suggested as the efficient synthesis method [2]. From this motivation, we demonstrated the direct interzeolite transformation of borosilicate MWW (B-MWW) as a parent material into the three different transition metal-based cobalt-, nickel-, and zincosilicate beta zeolites (Co-BEA, Ni-BEA, and Zn-BEA). Dried mother gel including calcined B-MWW, siliceous beta seed, TEAOH, metal nitrate solution, and NH4F was heated at 190 °C for different crystallization times. Calcined solid products of Me-BEAs after the interzeolite transformation were characterized by powder XRD, TGA/DTA, ICP-OES, SEM, (S)TEM-EDS, UV-DRS, XPS, IR spectroscopy. Then, we applied the fully crystallized Me-BEAs to the cascade conversion of glucose at 160 °C for 1–24 h. In the interzeolite transformation of B-MWW into Me-BEAs, the structural transformation of MWW to *BEA and the incorporation of framework heteroatoms independently proceeded depending on the type of framework metals. The structural transformation rate showed the order: Ni-BEA (< 1 day), Co-BEA (< 2 days), and Zn-BEA (< 7 days), which is depending on the solubility of BEA seed in the preparation step according to the pH value of each metal precursor solution: 9.68 (Ni-BEA) > 9.55 (Co-BEA) > 9.48 (Zn-BEA), because the dissolution of BEA seed provides common building units to accelerate the growth into the *BEA structure [3]. Interestingly, Co-BEA showed 0.8 wt.% of Co species in the initial stage, but Ni-BEA and Zn-BEA exhibited 2.6 wt.% of their framework metal species, which is not corresponding to the trend of structural formation. This is likely due to that the largest hydrated Co(H2O)62+ among three hydrated metal species due to the difference of atomic radius is the most difficult to access to vacant silanol nests to be formed by the extraction of B species in mildly acidic condition [4]. We also proved that TEA+ was the most essential factor for inducing *BEA structure and OH– had a critical role to produce enough sub-units to proceed the interzeolite transformation. Even though it was demonstrated by various characterizations that all metal species exist in the structures of Me-BEAs, those showed different chemical states of framework metal species: Co2+ : Coδ+ = 0.8 : 0.2 for Co-BEA, Ni2+ : Niδ+ = 0.6 : 0.4 for Ni-BEA, and only Zn2+ for Zn-BEA owing to the thermal stability of the structures containing Meδ+ of as-made samples, which resulted in the order of Lewis acidic property according to the concentration of most electron-deficient Meδ+: Ni-BEA > Co-BEA > Zn-BEA. These results directly catalyzed the cascade glucose conversion, thus, Ni-BEA exhibited the highest initial activity and Zn-BEA showed the highest 5-HMF yield due to the consecutive catalysis over the most concentrated weak Brønsted acidic silanols of Zn-BEA. From these comprehensive results, it can be experimentally demonstrated that the performance of heterogeneous catalyst is determined from the catalyst synthesis stage.

1052 - THE SYNTHESIS OF ULTRA THIN BPH NANOSHEETS WITH EXCEPTIONAL ADSORPTION PROPERTIES

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The transition of the global energy system from traditional fossil fuels to renewable and sustainable energies and processes necessitates the development of new and the re-invention of existing materials. Specifically, zeolites will play a key role in facilitating this transition due to their exceptional qualities which finds them applied in essential catalytic and adsorption processes such as carbon capture and storage. However, the zeolites employed in such processes are composed of particles of micrometre scale. As a consequence, a small molecule such as CO2 must diffuse a distance approximately tens of thousands of times its own size through the particle. In addition, the presence of structural imperfections and compositional inhomogeneity in combination with the relatively low surface-to-volume ratio of the micron-sized particle will limit the number of available active sites for adsorption and catalytic processes. This will also result in a relatively large mass transfer zone within a fixed bed configuration limiting the usable capacity in separation processes.

Nanozeolites offer several key advantages over their conventional micron-sized counterparts such as high surface-to-volume ratios providing greater access to more active sites, rapid diffusion properties, and rich silanol chemistry for the introduction of heteroatoms [1]. Furthermore, the direct synthesis using inorganic structure directing agents (SDA) ensures the formation of nanozeolites with uniform elemental composition and desirable adsorption properties that do not require post-synthetic calcination treatment.

In this presentation we describe the direct synthesis of ultra-thin BPH nanosheets from an alkali aluminosilicate colloidal precursor suspension using inorganic SDAs only at mild hydrothermal conditions (60 °C). By tailoring the ratio of alkali metal cations serving as inorganic SDAs the thickness of the BPH nanosheets is halved from approximately 10 to 5 nm and the Si/Al is slightly increased from 1.3 to 1.5 resulting in an improved thermal stability compared to our previous report [2]. N2 adsorption analysis reveals that the reduced thickness of the nanosheets imparts high interparticle mesoporosity to the zeolite which is reflected by its exceptional adsorption properties. Thermogravimetric analysis (TGA) of the as-synthesised ultra-thin BPH nanosheets reveals that the nanozeolite adsorbs an incredible amount of water, up to 50 wt%, the highest value of any zeolite material. Water isotherm analysis of the ultra-thin BPH nanosheets also shows that the high interparticle mesoporosity is responsible for the exceptional water adsorption performance due to the S-shaped isotherm. The nanosheets demonstrate significant water adsorption at relatively high humidity (RH > 65 %). This is corroborated by the TGA results whereby the majority of the weight loss, or desorption of water, occurs at temperatures below 100 °C. The diffusion properties of the ultra-thin BPH nanosheets were also explored by breakthrough curve analysis of CO2 revealing exceptionally sharp curves indicative of the rapid diffusion properties due to the ultra-thin morphology of the sheets. The unique adsorption properties of the ultra-thin BPH nanosheets makes them an interesting candidate for CO2 capture from humid streams.

Acknowledgements

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1121 - DEFECT MODIFICATION ON METAL ORGANIC FRAMEWORK UIO 66 VIA MODULATED SYNTHESIS FOR ALDOL CONDENSATION REACTION

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Introduction

UiO-66 (Zr) is an archetypal metal-organic frameworks (MOFs) consists of hexanuclear, octahedral zirconium oxoclusters (Zr6O8) connected through terephthalate linkers.[1-3] It attracted considerable attention in the large family of MOFs due to an easy lab-scale synthesis, relative high stability and various properties for applications. The properties of UiO-66 are influenced by the presence of missing linkers, known as defects.[4] Defect engineering is conducted via modulated synthesis, diverse modulators such as formic acid (FA), acetic acid (AA) and trifluoroacetic acid (TFA) were introduced during the synthesis.[5] The generated defect sites during synthesis provide catalytic activities for reactions such as aldol condensation.

Materials and Methods

UiO-66 samples with varies concentration of defects were prepared via modulated synthesis with certain amount of formic acid (FA) as modulator, respectively. The as-synthesized sample were activated in N2 flow at 523 K to remove the remaining DMF and FA in the pores. The samples are characterized by N2-adsorption, dissolution 1H NMR, IR spectroscopy. The concentration of the defect site was determined from thermogravimetric analysis together with acetone titration using calorimetry. The coordinational unsaturated Zr on the defect acts as Lewis acid sites showing high catalytic activity of aldol condensation reaction between furfural and acetone.

Results and Discussion

The concentration of defect sites on UiO-66 (Zr) can be modified via modulated synthesis using formic acid as a modulator (named as UiO-66-XX, being XX the moles of formic acid with respect to the moles of Zr in the synthesis). The concentration of defect sites were determined by calorimetry measurements absorbing acetone, which is turned to be a proper probe molecule for the titration of the defect sites on UiO-66, showing higher heat of adsorption as shown in Table 1.

The whole series of samples were then tested with aldol condensation reaction between furfural and acetone to form the primary product 4-(2-furyl)-4-hydroxy-2-butanone (product A for short) and condensed α,β-unsaturated product, 4-(2-furyl)-3-buten-2-one (product B for short). The results reported here demonstrate that the exposed Zr on the defect site acts as Lewis acid site catalyzing the aldol condensation reaction, showing high TOF. (Figure 1)

Significance

Our work advances the development of methods to titrate the concentration of defect sites using acetone as a probe molecule combining calorimetry and the activity of the defect sites catalyzing aldol condensation of furfural and acetone.

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1151 - DEVELOPMENT OF SILANOL DEFECT FREE TITANIUM SILICALITE 1 WITH ADVANCED CATALYTIC PERFORMANCE VIA DEFECT HEALING TREATMENT

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Titanium-silicalite-1 (TS-1) is an aluminum-free zeolite with MFI type framework [1]. As a high-performance catalyst in industry, TS-1 has received extensive attention from researchers for the past decades. Involving aqueous hydrogen peroxide as a green oxidant, TS-1 exhibits high activity and selectivity for oxidation reactions of considerable organic compounds [2]. It has been widely acknowledged that tetrahedrally coordinated titanium in the framework is the main active site [3]. Hydrogen peroxide attacks tetra-titanium to form Ti-OOH active species. As a result, epoxides are produced because of the directional oxidation of the C=C bond. However, the existence of silanol defects in the framework of TS-1 compromises its catalytic activity and leads to the formation of by-products. The defect-healing treatment proposed by Iyoki et al. [4] is widely employed to reduce structural defects in zeolite frameworks [5]. Herein, we optimized the defect-healing treatment for TS-1 to eliminate the internal silanol defects from the framework.

TS-1 samples with various Si/Ti ratios (70 to 50) were prepared via direct hydrothermal synthesis under 175 ºC for 24 hours [6]. Followed by defect-healing treatments involving ammonium fluoride and tetraethylammonium hydroxide, TS-1-healed samples were obtained. As confirmed with UV-vis, negligible extra-framework Ti was observed in both TS-1 and TS-1-healed samples. Successful elimination of silanol defects of TS-1-healed was demonstrated via FT-IR, 29Si single-pulse and CP MAS NMR. A significant improvement in the hydrophobicity of TS-1-healed was observed via static water vapor adsorption isotherms recorded at 25 ºC. The water vapor adsorption capacity decreased from 10.3 wt% to 6.5 wt% after the defect-healing treatment.

To evaluate the catalytic performance, epoxidation of 1-hexene with hydrogen peroxide was carried out in a closed environment under 60 ºC. With 50 mg catalyst, 10 mmol 1-hexene and 10 mmol hydrogen peroxide reacted in 10 ml methanol for 2 hours. For TS-1-50 (Si/Ti = 51.5), the conversion of 1-hexene was 26% and the selectivity of 1,2 epoxy hexane was 78% while TS-1-50-healed exhibits, an improved 1-hexene conversion of 44% with 79% selectivity of 1,2 epoxy hexane. It is worth noting here that the TS-1-50-healed showed comparable catalytic performance with that of a commercially available TS-1 (Si/Ti = 24.6) from ACS Materials (conversion of 47% with the selectivity of 85%). It is clear from this study that the proposed defect-healing treatment is not only promising for the significant advancements of hydrothermal stability of zeolites but also provides new insights into the preparation of high-performance zeolite catalysts.

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1159 - STABILIZATION OF PLATINUM CLUSTERS ON MONOLAYERS OF MWW ZEOLITE FROM LIQUID DISPERSION

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Rational functionalization and construction of zeolites nanocomposites has drawn much attention, due to their potential use in heterogeneous catalysis, energy storage and conversion, biological applications, etc. [1] Direct exfoliation of zeolites into colloidal suspensions of monolayers has widened the spectrum of novel zeolitic supports for functionalization, thus enabling possible design of novel composite materials for different applications, such as catalysis. Zeolites are used to encapsulate metal nanoparticles to improve the metal nanoparticles thermal stability which maintains their catalytic activity, while zeolitic structure can improve the selectivity of these catalysts towards target products. Metal@zeolites are an important class of catalysts for hydrogenation and dehydrogenation, reforming, water-gas shift reactions, etc. [2] In-situ encapsulation and post-synthesis functionalization are currently two main synthesis strategies for metal incorporation in zeolites. Yet, the obtained catalysts are mostly 3D crystals; thus, they usually suffer from mass transfer limitation due to narrow pore sizes and limited accessibility to the active sites. A possible synthesis strategy to overcome these issues is to utilize protective surfactant to introduce mesoporosity resulting in design and preparation of more open architectures. Exfoliated zeolite supports enable diverse applications, such as preparation of hierarchical materials that are promising catalysts for bulky molecules. [3] However, these novel supports are limited to the zeolite representatives that have been obtained as monolayer nanosheets in solution.

Herein, we utilize MWW zeolite monolayers colloidal suspensions, obtained by soft-chemical exfoliation, as supports for Pt clusters. Pt clusters were prepared with an average size of 1 nm and then, introduced via a wet-chemical homogeneous approach at room temperature. The use of MWW monolayers as a support allowed stabilization of small metal clusters at defined surface. We describe the structure and texture of support, as well as the size, location, and distribution of metal species in prepared Pt/MWW monolayer nanocomposites. X-ray diffraction (XRD) proved the preservation of MWW zeolitic layers structure, which was further confirmed by scanning transmission electron microscopy (STEM) imaging. Additionally, STEM results show that immobilized Pt clusters are well preserved and demonstrate a good thermal stability upon calcination, as well as under reaction conditions. The zeolite monolayers are stacked in disordered manner, resulting in a hierarchal structure of the Pt/MWW composites. We selected hydrogenation of cinnamaldehyde as a model reaction to explore the catalytic potential of the prepared Pt/MWW nanocomposite and compared it with 3-dimensional Pt@MCM-22 and Pt/MCM-22-imp (impregnated) materials previously reported.

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1269 - HYDRATED SILICATE IONIC LIQUIDS AS A PLATFORM FOR ORDERED AND NON ORDERED SILICATES

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Recent developments in inorganic zeolite sciences have refocused their attention on formation mechanisms [1-2]. Hydrated Silicate Ionic Liquids (HSILs) offer new opportunities for this endeavour thanks to their monophasic and, thus, more accessible nature [3]. Recently, the role and function of the cation have found attention: Ion association between the alkali cations and the aluminosilicate anions, have been observed to effectively stabilize oligomers [2], and function this way as precursors in zeolite crystallisation, as well as framework selection [4-5].

HSILs are inorganic hyper alkaline silicate liquids with minimal amounts of water. When doped with aluminate, they yield high-quality zeolites under mild conditions at high crystallization rates. The combination of high alkalinity and low water content forces the aluminosilicates into small, soluble oligomers resulting in an optically clear, homogeneous liquid, convenient for physicochemical investigation [3]. In different conditions, aluminosilicates can also condense in a non-ordered manner, forming Bragg-amorphous materials, often classified as geopolymers. These materials find attention as a potential replacement for Portland cement. Production of the latter is responsible for 8% of global carbon emissions, of which over 70% is inherent to its chemistry and thus unavoidable. Geopolymers have similar properties but do not suffer from these inherent carbon emissions. Unfortunately, their chemistry is not yet fully understood, so their full potential remains out of reach [6-7].

As the structural relationship between geopolymers and zeolites is evident, HSIL-based synthesis can bring clarity here too. HSILs are mixed with an aluminium source to form a paste that delivers solid monoliths upon drying. The water and aluminium content of the synthesis paste determine the water stability and degree of aluminium incorporation in the final product, two essential parameters. It is also possible to engage the chemical resemblance of zeolites and geopolymers differently: Treating geopolymers hydrothermally in alkaline solutions yields various zeolitic frameworks but preserves their macroscopic shape. This feature enables the production of self-supporting, tuneable and active materials. This synthesis approach readily yielded new zeolite-geopolymer composites and identified the conversion liquids' alkalinity, cation type, and silicon content structure-determining variables. Parallels with regular zeolite synthesis are omnipresent: The formed frameworks are cation-specific, and alkalinity and water content have the same influence as observed previously [4].

Geopolymer formation and their potential transformation into crystalline zeolites appear to follow the same mechanism of formation found for zeolite formation from HSILs. Figure 1 summarizes these observations. HSILs showing a high chemical potential when made (low alkalinity and elevated aluminium fraction) have a low energy barrier for condensation of aluminosilicates. This results in immediate, non-ordered condensation into geopolymers. Low chemical potential liquids require additional activation energy to cross the energy barrier. These liquids form crystalline, more stable zeolites. When given sufficient time and energy, the geopolymers can cross this boundary in an alkaline solution to (partially) transform into a crystalline zeolite lattice.

The presented research focuses on the solubility of the various components in function of temperature and batch stoichiometry, to evaluate under which circumstances crystalline zeolites or Bragg-amorphous geopolymers are formed.

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1284 - ZEOLITE TEMPLATED CARBON METAL SUPPORTED CATALYSTS FOR HETEROGENEOUS REACTIONS

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The inherent properties of a single atomic carbon layer in graphene offer opportunities for the creation of catalytically active centers tailored on a molecular level on a support with high thermal stability and very high specific surface area (~2600 m2 g-1). The wide range of means of functionalizing the graphene monolayer could be exploited in the development of heterogeneous catalysts with active sites controlled at the atomic level. However, utilization of the unique properties of graphene for application in a catalytic process relies on the development of a three-dimensional (3D) graphene-like catalytic material with connectivity of the pore network, providing good accessibility to the active sites. In this study, metal supported 3D graphene-like microporous carbons synthesized in the beta and faujasite zeolite templates, denoted as β-carbon and Y-carbon, respectively, were analysed with respect to their structure and catalytic properties in comparison with metal supported conventional catalytic materials.

Structural analyses showed that the β-carbon and Y-carbon are characterized by 3D assembled and highly stable single atomic graphene layers forming an open porous system resembling the regular channel system of the zeolites with a specific surface area comparable to the surface area of graphene (≥2500 m2 g-1) [1]. The curved surface of the 3D graphene-like structure having accessible porosity through the channel system is characterized by the presence of unsaturated carbon atoms at the edges, together with a tunable concentration of oxygen-containing functional (hydroxyl/phenolic and carboxyl) groups. The study demonstrates the potential of the 3D graphene-like materials for the preparation of metal catalysts with a very high concentration of well dispersed metal clusters of tuneable size. The metal clusters (Pt, Pd, Rh) were introduced into 3D graphene-like carbon materials as active centers for hydrogenation reactions. The relationships between catalytic properties and structural parameters including the effects of the size of metal clusters from a nanometre to a sub-nanometre scale, effects of the interactions of the metal-graphene support and reduced metal–metal coordination were analysed. The materials catalyse the hydrogenation of aromatics, alkenes, alkynes and cycloalkenes into the corresponding alkanes and cycloalkanes with exceptionally high reaction rates and selectivity.

Zeolite templated 3D graphene-like carbon catalysts represent a novel concept in the field of heterogeneous catalysis, which enables a dramatic increase in the surface area available for active centers and the tuning of catalysts functionality for a wide range of catalytic reactions for hydrogenation/dehydrogenation and processing of hydrocarbons. The results of the study illustrate a method for the exploitation of the unique properties of a single layer of carbon atoms in heterogeneous catalysts characterized by outstanding specific surface area and high thermal stability [1].

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1286 - SEED DIRECTED SYNTHESES OF ZEOLITES IN A VERSATILE BOROSILICATE SYSTEM WITH THE PRESENCE OF OCTYLTRIMETHYLAMMONIUM CHLORIDE

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Zeolites, as crystalline microporous materials, are formed by TO4 tetrahedra (T = Si, Al, B, Ge, P, Ga, Zn, etc.) that are connected to create various secondary building units (SBUs), which in turn are connected to form network-like frameworks [1]. The T atoms are important for the formation of n-membered rings (n-MRs), including 3~6-MRs, double 3-MRs and double 4MRs. Zeolites are usually crystallized in initial gels containing organic species, acting as (1) pore filler, (2) structure-directing agent, and (3) template [2]. Residual organic species in mother liquid may cause environmental pollution and increase of cost, therefore, parent zeolites or seed zeolites are usually employed to decrease or eliminate the use of organics in zeolite syntheses. Through zeolite-to-zeolite transformations, many valuable zeolites have been synthesized in the absence/presence of OSDAs with the presences of pre-crystallized zeolites as either main raw materials or seeds [3-4].

Seed-directed synthesis is an efficient method to obtain useful zeolites. It is still important to illustrate the structure-directing ability of seed. Herein, a comprehensive investigation on the crystallization of borosilicate zeolites with the presence of Octyltrimethylammonium Chloride (OTMAC) was performed by introducing seeds with different frameworks into the new constructed versatile Na-borosilicate system. Without OTMAC, the adopted Na2O-B2O3-SiO2 system was capable of synthesizing magadiite, a layered silicate with abundant 5-MRs. When OTMAC was added, MWW and *MRE zeolites were synthesized. By introducing both OTMAC and zeolite seeds of different structures (*MRE, SFE, IWV, MWW, MFI, ERI, EUO, MTT, TON), accompanied by adjusting crystallization time and the chemical compositions, a total of 14 seed-to-product zeolite pairs (including 9 isomorphic pairs) were obtained. Most seed-to-product zeolite pairs followed an increasing trend in FD. The seed-directed crystallizations were governed by the seed structures, and the gel compositions as well. There existed both weak and strong directing effect between the structures of seeds and products. For strong directing effect, there were similarities in n-MR distributions of the structures between products and seeds, which may act as the driving force for the crystallizations of certain structures that could be used to explain seed-directing syntheses of zeolites. Predictably, more types of zeolite products would be synthesized in the Naborosilicate-OSDA gel system by introducing seeds of other structures. Besides, the n-MR distribution-based analysis would, on some extent, provide us with quantitative information. Thus, it may be used to value the similarity between different structures and find a way to realize design synthesis of zeolite in the future.

1311 - SYNTHESIS OF FAU AND CHA TYPE ZEOLITES FROM CLASS C FLY ASH EFFECT OF ALKALINE AGENT AND SYNTHESIS CONDITIONS

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Zeolites are mainly porous aluminosilicate materials with open three-dimensional skeleton structures. Owing to their high specific surface area and excellent cation exchange capacity, zeolites have been used in various industrial fields such as water treatment, petrochemistry, gas purification, and flue gas cleaning [1]. The great demand for zeolite in the industry has accelerated research on producing zeolites using reduced-cost raw materials and eliminating other expensive chemicals such as OSDAs. One of the most promising raw materials for zeolite production is fly ash, which comes as waste from coal-fired power plants [2]. Although the synthesis of zeolite from class F fly ash (SiO2 + Al2O3 + Fe2O3 > 70) is extensively investigated in the literature, studies with class C fly ash (SiO2 + Al2O3 + Fe2O3 > 50) are very few. Besides low SiO2 and Al2O3 content, more impurity phases such as anhydrite (CaSO4) and hematite (Fe2O3) are found in class C fly ash, leading to undesired phases in zeolite formation. However, it was revealed that oxide impurities from fly ash could be eliminated by acid leaching [3]. In addition to the elimination of impurities, acid leaching also causes the dealumination of fly ash which could be beneficial for synthesizing high silica zeolites such as FAU and CHA.

This study aimed to investigate the synthesis of FAU and CHA-type zeolites from fly ash without additional sources (OSDAs, silica, and alumina sources). For this purpose, class C fly ash was leached with 5M HCl solution to remove the impurity phases (CaSO4 and Fe2O3) and increase the Si/Al ratio. XRF analysis results showed that SiO2 + Al2O3 content increased from 61.9% to 94.71%, and Si/Al molar ratio
increased from 1.31 to 2.85. From the XRD pattern of raw and optimized (5M HCl) acidified fly ashes (AFA), it was observed that acid leaching removed a large amount of anhydrite impurity from fly ash but had less influence on the hematite and quartz crystalline phases. The dissolution rate of quartz is lower than other phases; therefore, acid treatment did not affect the silicon content in the fly ash, and it transformed into an available silica source after alkaline fusion. AFA samples were subjected to alkali fusion and hydrothermal synthesis to synthesize zeolites using NaOH and KOH as alkaline agents at different synthesis conditions. XRD diffractograms of synthesized zeolites revealed that samples fused with NaOH converted to mostly FAU framework with a low amount of zeolite P (GIS) and LTA as impurity phases, and samples fused with KOH converted to CHA and zeolite W (MER) framework. In conclusion, crystallinity and percentage of desired zeolite phases in the structure are strongly dependent on the synthesis conditions.

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CATEGORY: AIR AND WATER CLEANING

1272 - HOW AMMONIA WATER OR OXYGEN AFFECT AT ADSORBED N2O ON DIFFERENT FE SPIECES IN ZSM 5 DFT STUDY FOR DEN2O PROCESS.

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Anthropogenically produced nitrogen oxides (NOx) are the source of many air pollutants such as acid rain and photochemical smog [1], threatening both human health and the environment. Nitrous oxide (N2O) is also a very serious harmful gas [2]. This oxide is produced during nitric acid production or as a by-product of the NH3-SCR process. This gas has a global warming potential (GWP) approximately 310 times higher than that of the much more well-known CO2 [3].

N2O molecules are formed during nitric acid synthesis and also as a by-product in the deNOx SCR process [4,5]. Due to the second aspect, catalysts that are effective in both deNOx and deN2O processes are being searched for. This will reduce costs, save space and time, which will significantly affect the efficiency of processes in which nitrogenous compounds play a major role. Studying the behaviour of the catalyst after N2O adsorption in the presence of molecules involved in the deNOx process is a first step for understanding the mechanism of the deN2O process.

In the present study, the zeolite ZSM-5 with Fe adsorbates deposited on surface was proposed as a catalyst for the deNOx and deN2O processes. It is important to note that iron can exist in the pores as mono-, bi- or oligomers, and also as oxides or different species [6]. This paper presents the effects of molecules such as ammonia, water and oxygen on the zeolite catalyst ZSM-5. During the synthesis of the Fe-ZSM-5 catalyst, various iron adsorbates - Fe, FeO, Fe2O or Fe2O-OH - are deposited on the surface as potential active centres. Energy analyses of N2O adsorption to the proposed structures were performed, followed by energy analyses of systems with additional molecules. Calculations were performed using Density Functional Theory (DFT) based on an ab initio method. The analyses also included the analysis of charges, bond orders and bond lengths.

The research has provided a better understanding of how the molecules present in the SCR process can influence each other. Charges, bond lengths and bond orders have allowed a detailed electron description of the systems obtained, which further supports the possibility of predicting next changes. The analyses presented here are a prelude to investigating the mechanism of the deN2O process in combination with the deNOx process.

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CATEGORY: BIOAPPLICATIONS

1084 - SYNTHESIS OF BIO JET FUEL PRECURSORS THROUGH FURFURAL AND CYCLOPENTANONE ALDOL CONDENSATION USING METAL OXIDES DEPOSITED OVER N ZSM 5 ZEOLITE

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The production of advanced biofuels to be used in the formulation of jet fuels appears as one of the main priorities for the decarbonization of the transport sector [1]. Aldol condensation of green aldehydes and ketones is one of the most promising reactions to increase the number of carbons presented in the final biofuel [2]. Thus, furfural (FFL) and cyclopentanone (CPO) are produced via lignocellulosic biomass pyrolysis and can be converted into larger molecules with 10 and 15 carbons via aldol condensation. Recent efforts have been devoted to develop selective and active catalysts highlighting those with basic properties. However, the use of acid materials, such as crystalline zeolites, has been scarcely explored [3].

In this work, FFL and CPO aldol condensation was performed at temperatures of 80 and 100 ºC, and reactants CPO:FFL molar ratio of 6:1 and 10:1. Wet impregnation method was used to incorporate 10 wt.% of different basic (MgO and CaO) and acid (TiO2, ZrO2 and SnO) metal oxides over nanocrystalline ZSM-5 zeolite (n - ZSM-5, Si/Al=42, Clariant CZP90). The tests were performed in a StarFish reaction system with 0.2 g of catalyst. Samples were taken at different times (2, 4 and 6 h) and were diluted in a mixture of mesitylene (internal standard) and ethyl acetate (solvent), to be analysed quantitively by GC-FID.

The CaO and MgO-containing catalysts led to FFL conversion values even lower than those obtained with the parent zeolite, showing that the incorporation of basic components does not benefit the catalytic activity of n - ZSM-5 zeolite. Likewise, these materials promoted the formation of C10-OH instead of the desired dehydrated C10 species. These findings can be linked with the strong decrease observed in the zeolite acidity after Ca and Mg addition due to both cation-exchange and micropore blocking effects.

In contrast, modification of the parent n-ZSM-5 zeolite with metal oxides having acidic features produces significant improvements in the reaction. Thus, at 80 ºC, the highest FFL conversion was observed when using TiO2/n-ZSM- 5 (14.5%) at 10:1 molar ratio, and the best selectivity towards C10 with SnO/n-ZSM-5 (92%). The increase in the temperature to 100 ºC (10:1) further enhances the catalytic activity reaching a FFL conversion of 40 and 25% over TiO2/n-ZSM-5, whereas the highest C10 selectivity (85%) is again obtained over SnO/n-ZSM-5. Regarding ZrO2/n-ZSM-5, FFL conversion is intermediate (25%) while the production of C10-OH is promoted obtaining the highest selectivity value (60%).

It can be concluded that modifying the n-ZSM-5 zeolite through the incorporation of acid metal oxides, providing additional Lewis acidity that complement the Bronsted acid sites, is an interesting strategy to improve the zeolite catalytic activity and selectivity in FFL-CPO aldol condensation.

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1268 - DUAL FUNCTIONAL POROUS SOLID ACIDS WITH ENHANCED ACTIVITY AND STABILITY FOR TRANSFORMATION OF GLUCOSE TO 5 HYDROXYMETHYLFURFURAL

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Introduction. 5-Hydroxymethylfurfural (HMF), which can be derived from biomass, is one of the most vital building blocks with a global production capacity of 5,000-10,000 tons per year [1]. Recent studies have attempted to transform glucose into HMF using solid acid catalysts with controllable acid sites, improving HMF yield and reducing environmental pollution. In this study, the dual functional SBA-15 mesoporous silica (denoted as Al-SA-S15), which contained various loadings of aluminium (Al) and sulfonic acids (SA) as Lewis and Brønsted acids, respectively, gave high activity in conversion of gluclose and high yield toward HMF using a co-solvent of H2O and acetone. Among them, the Al-SA-S15 catalyst with a Si/Al molar ratio of 5 and a SA loading of 15 mol.% gave a 95% conversion of glucose and 51% of HMF yield at 160 ºC for 4 h. Its high performance was remained unchanged after recycle and reuse for 5 times.

Experimental/methodology. The Al-SA-S15 catalysts were prepared by direct synthesis route and used in the transformation of glucose to HMF in an aqueous solution with adding acetone at 160 ºC for up to 5 h. The prepared catalysts were characterized by N2 physisorption, CHNS elemental analyzer (EA) and inductively coupled plasma-optical emission spectroscopy (ICP-OES). The catalytic reaction was performed in a 15 mL ACE pressure tube. The products were analyzed by an HPLC (Agilent 1260 Infinity II) instrument equipped with an Aminex HPX-87H column.

Results and discussion. The 5Al-15SA-S15 catalyst with a Si/Al molar ratio of 5 and a SA loading of 15 mol.% , analyzed by EA and ICP-OES methods, was highly active in conversion of glucose to HMF with a yield of 51% at 160 ºC for 4 h (Table 1 and Fig. 1). This catalyst was easily regenerated by washing the used catalyst with acetone, and the performance of regenerated catalyst was nearly unchanged after being reused for at least five times. Characterization results indicated that the structural properties and the loadings of Al and SA of as-prepared and regenerated catalysts were close to each other. This indicates that the Al-SA-S15 catalyst was highly active and stable in glucose transformation to HMF with a high yield and regenerable under the studied conditions.

CATEGORY: COMPUTATIONAL APPROACHES IN POROUS MATERIALS RESEARCH

1046 - MICROSCOPIC ORIGINS OF THE XENON KRYPTON SEPARATION IN MOFS

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Nanoporous framework materials are a promising class of materials for energy-efficient technology of xenon/krypton separation by physisorption. Many studies on Xe/Kr separation by adsorption have focused on the determination of structure/property relationships, the description of theoretical limits of performance, and the identification of top-performing materials. Here we present novel methods to speed up the determination of these characteristics using faster simulation algorithms.

To better understand the xenon/krypton separation process, an early study focused on the thermodynamic performances of 12,020 Metal-organic Frameworks from the CoRE MOF 2019 database at different pressure conditions [1]. We found out that the xenon adsorption enthalpy plays a key role in determining the most selective materials, thus highlighting the underlying enthalpic nature of the separation process. Furthermore, for selective materials, the selectivity can drop when we increase the pressure from the infinite dilution to the ambient pressure due to the diversity of the adsorption pores and the reorganisation within the channels of the materials. Further studies on the reasons behind this selectivity drop can help to understand and predict it, thus avoiding heavy GCMC calculation in screenings.

Based on the previous findings, we focused on finding faster ways of calculating adsorption energies as a way of characterizing materials for separation. We developed a new algorithm that calculates the adsorption enthalpy and the Henry constant by sampling the pore surfaces of the nanoporous materials [2]. This newly implemented C++ code is proven to be accurate (error of 0.34 kJ/mol on the enthalpy) and much faster (about 0.3 s per structure) than the standard Raspa implementation of Widom's insertion and opens the possibility to analyze bigger databases via direct high-throughput screenings or via machine learning based ones.

During the studies of extremely promising materials like SBMOF-1 [3], we were puzzled by the difference between the predicted theoretical selectivity (70.6) and the experimental one (16). This difference can come from the rather unprecise multipurpose forcefield used, but also from more fundamental physical reasons such as the flexibility of the material or the transport effects (kinetic limitations). The diffusion of xenon was found to be extremely limited in the channels of SBMOF-1. Therefore, we decided to explore potential kinetic limitations of the most selective materials and to uncover Xe/Kr selective materials with good xenon diffusion rates. This is very different from the Kr/Xe permselectivity screenings that are commonly done in the literature and is more applied to the development of separation membranes [4]. Our screening of the top Xe/Kr selective materials from CoREMOF 2019 identified some materials with a good selectivity coupled with a decent diffusion coefficients ratio. Furthermore, one of these materials have a higher diffusivity for xenon than for krypton, which is a priori counter-intuitive considering the differences of size. This phenomenon can be explained by the complexity of the channel geometries and is a yet undocumented mechanism to the best of our knowledge.

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1067 - COMPUTATIONAL AIDED DEVELOPMENT OF MOFS FOR THE CAPTURE OF POLAR VOLATILE ORGANIC COMPOUNDS

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Volatile Organic Compounds (VOCs) are air pollutants that compromise substantially indoor air quality. Adsorption-based processes can be effectively used to remove VOCs from air with the use of optimum adsorbents [1]. However, the presence of water poses an enormous challenge for the effective removal of highly polar VOCs with adsorbents, since water competes with the organic molecules for the occupancy of the pores. Simply designing hydrophobic porous adsorbents is generally not sufficient to effectively remove polar VOCs due to the lack of surface affinity for these compounds that are present in lower concentrations. Benchmark adsorbents for the capture of polar VOCS include zeolites and activated carbons [2] but their high-water affinity and/or moderate acetic acid selectivity hampers their efficiency in real conditions. Metal-Organic Frameworks (MOFs) have recently been proposed as potential alternatives for the capture of VOCs [3]. These highly tunable hybrids crystalline micro- or meso-porous solids exhibit several key features for the capture of VOCs such as high surface area, variable pore size/shape and hydrophilic/hydrophobic balance usually associated with mild regeneration conditions. Thus, for a given VOC capture application, ideal MOF adsorbents might be designed. Herein, we devised a computational strategy integrating Density Functional Theory calculations and force field Monte Carlo simulations to screen a series of MOFs for the selective capture of acetic acid in the presence of water. The knowledge gained from this computational effort led to the identification of two possible strategies to fine tune either hydrophobic or hydrophilic MOFs encompassing high affinity (Henry constant and adsorption enthalpy) for acetic acid, large acetic acid uptake at low concentration and importantly high acetic acid/water selectivity. We demonstrated that the insertion of -CF3 functionalized linker in the MIL-53(Al) framework enables a subtle combination of hydrophobicity and high acetic acid adsorption affinity/large acetic acid uptake. This prediction was completed by the synthesis of the corresponding MOF and breakthrough curve experiments confirmed its excellent performance that surpasses the best hydrophobic MOFs and other families of porous solids reported so far. Alternatively, this synergistic computational-experimental study revealed the hydrophilic MIL-100(Fe), bearing a high concentration of open metal sites (OMS), as an excellent candidate for the selective capture of acetic acid in the presence of water owing to an extremely high acetic acid adsorption enthalpy resulting from a direct coordination of the VOC on the OMS, resulting to a level of capture performance by far exceeding that of all family of porous solids tested so far.

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CATEGORY: CONVERSION AND STORAGE OF ENERGY

1104 - ACTIVATION OF MOLECULAR OXYGEN OVER BINUCLEAR IRON SITES IN CHA

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A recent study showed that binuclear Fe(II) sites in zeolite of FER topology exhibit the unique ability to split molecular oxygen with the formation of α-oxygen species. Formed α-oxygen possesses an outstanding activity in the oxidation of CH4 already at ambient temperature. Moreover, the products of this reaction were detected in the gas stream without an additional extraction step [1]. According to the current state of art, to form binuclear sites in the zeolitic matrix, a high population of closely located Al atoms (Al pairs), which stabilize divalent cations is required, as well as an axial geometry of two the cationic sites distanced by ~7Å. [1,2] However, this structural condition strongly limits the variety of zeolitic topologies efficient in the activation of O2. The aim of this contribution was to investigate the ability of zeolites with non-axial coordination of Fe(II) sites to split O2 and subsequently oxidize CH4. For the study zeolite of CHA topology was chosen due to its low Si/Al guaranteeing a high population of Al pairs, enhancing the potential formation of binuclear sites, and sufficient distance between iron sites.

DFT calculations (VASP program) including molecular dynamics were used to veryfy the possibility of O2 splitting over iron sites in zeolites of CHA topology. CHA sample (Si/Al 2.1) was synthesized with the template-free procedure [3], and iron was introduced to the sample by the impregnation with an acetylacetonate solution of FeCl3. Mössbauer and XAS spectroscopies were used to study the speciation and redox properties of iron sites after the evacuation of the zeolite at 450 °C, interaction with O2, and subsequent reaction with CH4 (as a testing reaction) at moderated temperatures (RT-220 °C). The activity tests in CH4 oxidation were performed at various oxidation times and temperatures in three consecutive redox cycles with mass spectrometry detection of the reaction products. Synthetized Fe-CHA (Fe/Al XX) sample possesses typical structural parameters for zeolite of CHA topology (XRD, SEM), and the exclusive presence of framework Al atoms (27Al MAS NMR). The results of Mössbauer and XAS studies point to atomically dispersed Fe(II) cations in the evacuated sample. Obtained spectral characteristics confirmed that the interaction of iron sites in CHA with O2 led to changes in the oxidation state of iron, which was subsequently reduced by CH4. The analysis of the oxidation products revealed the presence of CO2 and methanol detected directly in the gas stream. Moreover, the Fe-CHA works effectively in three consecutive reaction cycles. Gathered data allows the selection of optimal reaction conditions in order to obtain the highest productivity of oxygenates. The results of this pioneering study confirm DFT predictions, proving that O2 can be efficiently activated over binuclear iron sites in CHA and further applied for the oxidation of such inert molecule as CH4. Despite carrying the reaction over narrow-pored CHA topology, the oxidation products desorbed spontaneously from zeolite channels.

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1109 - DIFFERENCES OF SELECTIVITY IN CONVERTING CARBOHYDRATES WITH LEWIS ACIDIC ZEOLITES

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Lignocellulosic biomass has raised interest for the the production of platform molecules[1]. Carbohydrates such as glucose, fructose or xylose can be transformed to obtain valuable products, such as furanic compounds and organic acids. Nevertheless, the catalytic processes involve a complex reaction scheme, and the selectivity strongly depends on the substrate and on the catalyst. Zeolites with transition metals in the structure, especially Sn-BETA, have shown good activity for glucose isomerization.[2] However, while the specific case of glucose isomerization on Sn-BETA is mechanistically understood,[3] the other reaction pathways such as retro-aldolization, dehydration to organic acids have been less well elucidated. Likewise, the influence of different Lewis acidic sites (metals)[4] or of the substrate (sugar) has been scarcely examined so far. Herein, we study the selectivity of the reactions of transformation of biomass-based carbohydrates over different Lewis acidic zeolites.
We first prepared and characterized a series of catalysts. A commercial beta zeolite was dealuminated by a strong acid. The treatment decreased the aluminum content in the material from Si/Al =13 to about 200 with no structural or textural modification. Once dealuminated, different metals (Sn, W, Zr and Hf) were incorporated in the structure, targeting a content of 1% wt. Different preparation methods were compared, i.e., Solid State Ion Exchange (SSIE) or Equilibrium Adsorption in a solvent (water or isopropanol, EAW or EAI, respectively). The meso/microporosity was not altered by the different treatments. The incorporation of Sn by EAI failed (Sn < 0.02 %wt.) but SSIE and EAW showed no oxide presence with 1%wt Sn. W incorporated by SSIE revealed the presence of oxide phase; EAW exhibited a low adsorption capacity (only 0.33% wt. W). Zr incorporated by EAI led to oxide formation. In other cases, the targeted metal content was obtained without formation of oxide phases. We additionally employed UV-visible spectroscopy to confirm the grafting of isolated atoms into the zeolite structure.
For the catalysts displaying successful incorporation, the reactivity of glucose, fructose and xylose was studied and compared at two different temperatures (95 °C and 150 °C) in aqueous medium (40 bar N2). The W-incorporated materials afforded mannose in the conversion of glucose (epimerization product), but the analysis of the solution showed a near total leaching of the metal in solution during the reaction. Sn-BETA, Hf-BETA and Zr-BETA could selectively convert glucose into fructose, although Sn-BETA proved much more active. In all cases, little-to-no selectivity towards retro-aldolization of glucose was observed (formation of glycolaldehyde or erythrose). On the opposite, the conversion of fructose and xylose led to significant rates of formation of retro-aldolization products with Sn-BETA. The formation of organic acids (lactic acid) is also observed with these substrates. This study reveals that the metal could drive the reaction selectivity, carbohydrates with the same carbon number but not same configuration lead to different reactivity.

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1296 - METHANE DEHYDROAROMATIZATION ON MO ZSM 5 “DONUT” LIKE CATALYSTS

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Natural gas is a key resource for the energy transition from fossil to green production. Methane is the major component, and its transformation through the methane dehydroaromatization (MDA) reaction offers an attractive way to produce valuable aromatics and hydrogen. The MDA reaction is carried out at 700 °C on bi-functional Mo/HZSM 5 catalysts and allows a selective production of benzene (≈ 70 %) and hydrogen [1]. However, MDA development is hindered by two major drawbacks: (i) a low activity due to the thermodynamic limit of benzene formation at 700 °C (12.5 %) and (ii) the catalyst deactivation due to coke formation and irreversible damages [2].

The present work assesses the impact of diffusion path reduction by crystal core removal on the MDA reaction. A parent zeolite (ZP) with a silicalite-1 core surrounded by ZSM-5 crystal was synthesized through the seed-assisted method in F- medium, using nanosized silicalite-1 seeds. Then, ZP was subjected to two different treatments: NH4F etching (ZF) and alkaline leaching (ZOH). Both treated materials exhibit a hierarchical “donut”-like structure with mesopores connected to a central hole. The NH4F treatment led to an almost silanols-free material and alkaline leaching to the creation of additional small intracrystalline mesopores and external silanols. Finally, 3.5 wt.% of molybdenum was loaded by impregnation on ZP (Mo-ZP), ZF (Mo-ZF) and ZOH (Mo-ZOH) materials.

MDA reaction was carried out at 700 °C and atmospheric pressure on molybdenum-containing materials. The diffusion path reduction through “donuts”-shaping mitigates the catalyst deactivation while improving the benzene production. Furthermore, introducing a mesopores network on ZF and ZOH modifies the coke nature and shifts its location from the microporosity towards the mesoporosity. The coke retention in Mo-ZOH mesoporosity is enhanced by the silanols defects, acting as coke traps [3], with no impact on the activity and deactivation. Thus, only the coke in the microporosity deactivates the catalyst, while the coke deposited in the mesoporosity is a spectator of the MDA reaction.

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CATEGORY: DECARBONIZATION AND CO2 MANAGEMENT

1188 - REACTANT SHAPE SELECTIVITY FOR POLYOLEFIN PYROLYSIS CATALYZED BY ZEOLITE

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Towards sustainable society, chemical recycling of a polyolefin such as polypropylene (PP) should be important. The use of hydrocarbons as a solvent provides some advantages for the pretreatment of waste plastic and catalytic pyrolysis of PP over a solid acid catalyst. However, usually the hydrocarbon solvent is also consumed by catalytic cracking on the acid catalyst. We here report reactant shape selectivity due to the diameters of solvent molecule and pores of catalyst. A potential of selective pyrolysis of polyolefin with recycle use of solvent is demonstrated, and proceeding of the PP pyrolysis in micropores is clarified.

Silica-base (alkaline) treatments were performed for MFI type zeolite (EX-122 from Mizusawa Industrial Chemicals, Ltd.) according to Wakihara et al. [1] NaOH was dissolved into ion-exchanged water, and SiO2 (Tokuyama, Reolosil) and the MFI zeolite were added, heated at 453 K for 2 h with stirring, filtered, washed and dried, followed by ion exchange with NH4NO3 and calcination at 813 K to give SB-MFI. Base (alkaline) treatments were also carried out without SiO2 at 363 K for 0.25 h to give B-MFI. Beta type zeolite (HSZ-930 NHA from Tosoh Corp., calcined at 773 K) and an amorphous silica-alumina (N631-L from JGC Catalysts and Chemicals, hereafter ASA) were also employed. In a stainless steel batch reactor with a volume of 3.6 cm3, 0.05−0.1 g of the catalyst, 0.25 g of PP (JPEC, MW:370,000) and 1 g of solvent were put, the gas phase was purged with nitrogen, and the reaction was carried out for 1 h under mechanical vibration. After the reaction, the gas and liquid products were analyzed by an FID-GC and 2D-FID-GC, separately. The solid was washed, dried and weighed. The conversion of PP is defined as the loss of solid polymer.

In cyclooctane solvent on MFI type zeolite-based catalysts (MFI and SB-MFI) at 673−723 K, the conversion of solvent itself was <4 %, while PP conversion was 28−84% varied with the conditions. Thus, most of solvent is recovered, indicating the possibility of recycle use of solvent. In contrast, cyclooctane reacted well on Beta and ASA. In hexadecane on SB-MFI, the solvent hexadecane reacted well. Generally low PP conversion was observed in the combination of solvent and catalyst where the solvent conversion was high. Since the diameters are estimated to be hexadecane < PP < 10-ring channel of MFI < cyclooctane < 12-ring channel of Beta < mesopores of ASA, it is clear that cyclooctane did not penetrate into the micropore of MFI resulting in the reactant shape selectivity.

The influence of amount of NaOH employed for the base treatments showed that activity for 1,3,5-triisopropylbenzene cracking, showing the activity of Brønsted acid sites on the external surface, on B-MFI and SB-MFI was increased mainly in small NaOH amount region. On the contrary, the external surface area was increased in the large NaOH amount region. The PP conversion increased in the large NaOH amount region, and was well correlated with the external surface area, indicating that the PP pyrolysis did not mainly proceeded on the external surface but mainy proceeded in the region near to the pore entrances inside the micropores.

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CATEGORY: OPERANDO INVESTIGATIONS

1032 - EVIDENCE FOR THE ROLE OF RADICALS IN THE SYNTHESIS OF ZEOLITE TEMPLATED CARBONS A NEW APPROACH AT THE SOLID STATE

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Zeolite Templated Carbons (ZTCs) are carbon-based materials that are generated by the use of sacrificial zeolite templates. This materials family outstands through their unique properties combining electrical conductivity and tailored topology of micropores. While many gaseous and liquid carbonaceous precursors have already been used [1, 2], we describe for the first time the use of a solid carbonaceous precursor for the synthesis of carbonaceous ZTC materials having the same morphology as the model zeolite. This study aims to understand the different steps in the formation of ZTC materials from the simple mixture of solid anthracene and USY (Si/Al =2.6) as host material. Firstly, the filling of the zeolite micropores is carried out by the incorporation by sublimation of anthracene, linear molecules of adequate size, which ionize spontaneously in the internal volume [3]. Charge separation and radicals evolution within the porosity are followed using diffuse reflectance UV-vis absorption Raman scattering and EPR spectroscopy. The crucial role of these radicals reacting with each other by condensation to form larger polyaromatic compounds is particularly highlighted. The growth of the carbon skeleton was found to follow a cyclic behavior in which radical generation and recombination occur. Then, a heat treatment at 700, 800, 900 or 1000 °C was applied to the resulting Anth@FAU precursors to prepare the hybrid materials. The ZTCs were finally obtained for each of the hybrid materials after complete dissolution of the zeolite in an aqueous solution of HF. The samples were fully characterized using X-Ray powder diffraction, thermogravimetric analysis, nitrogen physisorption, electron microscopy, electrical conductivity measurements and Raman spectroscopy.
Regardless of the temperature applied during the heat treatment between 700 and 1000°C, the carbonaceous replicas obtained have similar morphological, textural and structural properties, although the use of high temperatures seems to favor a better condensation of the aromatic species present in the zeolite porosity. Nevertheless, due to larger kinetic diameter and sterical constraints of the anthracene molecule with respect to the internal microporosity, the entire internal volume of the zeolite could probably not be homogeneously filled and small filling defects might be present. Hence incomplete skeletal condensation could be deduced which results in ZTC with relatively low electrical conductivity. Although only a weak structural long-range order was observed for ZTCs, this new synthesis approach proves to be efficient and should be further developed using more flexible molecules.

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1266 - MOVING ELECTRODE ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY FOR IN SITU ZEOLITE CRYSTALLISATION MONITORING

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Probing the kinetics of crystallisation is important to understand and ultimately control crystal formation. Common experimental techniques frequently rely on time- and resource-consuming pre- and post-synthesis steps, which can alter the sample properties and increase the risk of measurement errors. Non-invasive, in situ methods are favoured but usually require expensive equipment and data analysis often relies on bold assumptions, which can lead to misinterpretation of the results. In the case of zeolites, studying the crystallisation behaviour is specifically aggravated, on the one hand, due to their complex formation mechanisms and, on the other hand, due to the nature of the synthesis medium - mostly heterogeneous, highly alkaline sols or gels - which are incompatible with most in situ characterisation techniques.

Zeolite synthesis from inorganic hydrated silicate ionic liquids (HSILs) has recently opened new perspectives in zeolite research [1]. These concentrated alkaline liquids consist of highly deprotonated, low-nuclear, and hypo-hydrated silicate oligomers in intimate interaction with alkali cations. In contrast to gels or sols, HSILs are homogenous and optically transparent. By adding aluminate to these mixtures, zeolites form within hours to days, even at low temperatures. As revealed in recent studies of our groups [2-4], zeolites in HSIL synthesis media are phase-pure, promoting a high signal-to-noise ratio. Furthermore, the high charge density in HSIL synthesis media and the associated specific condensation reactions qualify these liquids for electrochemical characterisation. For this purpose, a novel electrochemical measurement concept, specifically suited for corrosive samples has been developed: Moving electrode electrochemical impedance spectroscopy (MEEIS).

In contrast to classical impedance spectroscopy, where the sample is contained between two electrodes at a fixed position, MEEIS features a movable electrode mounted on a motorised linear stage to precisely adjust the inter-electrode distance. This way, electrical properties, such as electrolytic conductivity, can be determined from the change of impedance as a function of the electrode distance instead of the absolute impedance value [5]. This offers several advantages: (1) Specific sections of the sample can be probed independently, (2) static and quasi-static impedance contributions, for instance, from passivating material deposits at the electrodes, are eliminated, and (3) the movement of the electrode can be utilised to remove unwanted gas bubbles, frequently encountered in aqueous systems. Combined with temperature and corrosion-resistant materials, this method thus enables accurate in situ conductivity measurements in harsh chemical conditions.

Using MEEIS to monitor different HSIL systems reveals that zeolite formation is accompanied by the release of highly mobile ions, thereby proportionally increasing the conductivity of the synthesis medium. Conductivity changes are small but can be accurately resolved with MEEIS over long time periods, thus enabling convenient assessment of the crystallisation behaviour. Comparison to conventional conductivity measurements highlights the importance of a moving electrode approach, as passivation or sedimentation effects can have a detrimental effect on the measurement accuracy, rendering the data useless for further analysis. With MEEIS, on the contrary, accuracy is not affected by such spurious processes, qualifying this method as a robust tool for long-term in situ monitoring of corrosive fluids.

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CATEGORY: SEPARATIONS

1226 - DYNAMIC ADSORPTION OF CO2 N2 AND CO2 CH4 ON CATION EXCHANGED GISMONDINE A BREAKTHROUGH ANALYSIS

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The small-pore zeolites are considered primary candidates for the separation of small molecules (e.g., H2, CO2, N2, CH4, H2O, etc.) owing to their small pore size (3.0 – 4.5 Å) [1]. They are expected to play a central role in the selective adsorption of CO2 from the flue and natural gas (CO2/N2, CO2/CH4) since the adsorption capacity, and selectivity can be tuned through in situ or post-synthesis methods. Among them, NaP1 gismondine (GIS) type zeolite, exhibiting a topology with an eight-member ring pore opening and a pore diameter of 3.0 Å, appears ideal for the adsorption and separation of small molecules [2]. Herein, we present a template-free synthesis of high silica P1 zeolite. Further, the adsorption properties of the zeolites were modified by ion exchange with divalent cations such as Ca2+ and Mg2+.
A particular focus is set on breakthrough curve analysis, a technique allowing to obtain a realistic working capacity and selectivity data in industrially relevant conditions. Based on the breakthrough results, better CO2 separation performance was found for the parent zeolite Na-GIS. This behavior was attributed to the cooperative cation gating and gate breathing effect [3]. Lower selectivity was observed in the case of Mg and Ca exchanged GIS which might be related to the cation charge and its content and location within the GIS framework. Moreover, a critical aspect, which isoften overlooked, concerns the desorption behavior of CO2 in zeolites. Our data revealed that 95% CO2 desorption under 100% He flow is faster in Ca-GIS at 25°C (47 min) as compared to Mg- and Na-GIS (65 and 66 min, respectively). These results shed new light on the compromise between capacity, selectivity, and cyclability, being key factors in industrial processes. Furthermore, our preliminary results also validate the potential of GIS zeolites in fast cycling for efficient CO2 separation for both CO2/CH4 and CO2/N2 binary systems.

Figure 1: (a) CO2/N2 and (b) CO2/CH4 breakthrough curves on Na-, Ca- and Mg-GIS-3.0 using (CO2/N2/He, 5/25/70) and (CO2/CH4/He, 20/30/50) gas mixtures with a total gas flow rate of 40 and 20 mL min−1 at 25 °C, respectively. (c) CO2 desorption curves using 40 mL.min-1 of He at 25 °C.

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1144 - TUNING SIZE AND PROPERTIES OF BIONICS 1 FRAMEWORK VIA ACID MODULATION

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One of the biggest advantage of metal organic frameworks is the possibility of modification of their properties and tuning their inherent activity (ie. sorption, storage, catalytic activity etc.). Textural properties can be tuned by manipulating process and compositional parameters, among which, the effect of additives can be even further distinguished among themselves based on the way they affect these properties.We recognize (i) blocking agents that slow down or manipulate crystal growth in a certain direction by adsorption on a certain crystal face and so control crystal morphology; (ii) surface capping agents, that usually stop or inhibit further crystal growth; and

(iii) modulators, whose role is to control size and morphology by competing with organic linkers in order to coordinate with the metal ions during nucleation and growth process[1]. Beyond the effect that additives have on the size and/or morphology of nanoMOF, there is also an evident effect on properties via creating point defects – missing linker, missing node, modified linker or modified node defects. Defects are "sites that locally break the regular periodic arrangement of atoms or ions of the crystalline parent framework because of missing or dislocated atoms or ions" [2].

In this study, we investigate the effect of four monotopic acids – formic, acetic, dichloroacetic and propionic acid, their concentration and the heating type (conventional and microwave – MW) on the size, morphology and textural properties of a recently discovered zinc ascorbate MOF structure, denoted bioNICS1. bioNICS-1 is a bioMOF with permanent microporosity and bio-compatible constituents that has inherent potential in biomedical field as a drug delivery system[3] . Tuning of textural properties and controlled generation of acid

sites via point defect was achieved by utilizing simple monocarboxylic acids as a way of manipulating compositional parameter of synthesis. We confirmed that with the right choice of an additive and its concentration we can control the size of the crystallites according to seesaw model, and in the case of dichloroacetic acid also surface morphology. In the case of conventional heating, additives act as surface capping agents and blocking agents, whilst in the case of microwave synthesis their role changes to modulators. This was proved specifically in the case of propionic acid where missing node defects were observed, resulting in generation of additional acid sites. Generation of such sites is in great interest as it provides additional sites for chemisorption of therapeutic gas – nitric oxide [4]. With this study, tunability of bioNICS1 framework was proven, increasing its value as a candidate for drug delivery system.

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1154 - ZEOLITES “LOCAL REDOX POTENTIAL” BY STUDYING PHOTOELECTRON TRANSFER ACCORDING TO THE MARCUS THEORY

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Photoinduced electron-transfer (PET) processes are of fundamental importance in photochemical processes of biological and chemical systems. The ability to induce and maintain the charge separated states (CSS) is essential for the vitality of artificial light energy harvesting systems and then, the possibility of stabilizing sufficiently long CSSs to reduce the back electron transfer is essential. In order to slow down the rate of the recombination reactions, the use of confined media such as zeolites seems to be a promising way [1]. Zeolites are crystalline microporous aluminosilicates with a regular structure composed of channels and cavities of molecular dimensions. Thus, the internal pore volume of such dehydrated host material can easily accommodate guest molecules. The substitution of Al(III) for Si(IV) in the zeolite framework requires charge compensating extra framework cations M+ to ensure the charge neutrality. The aim of our study is to identify the parameters allowing a chemical control and a tunable lifetime of the CSSs using two probe molecule and various zeolite structures and compositions. The first probe molecule is 1,6-dipheny-1,3,5-hexatriene (DPH) which is known to generate radical cation upon UV photoexcitation [2]. The second probe is the 1,4 dicyanobenzene (DCB) well-known to generate radical anion under photoexcitation.

Previous studies showed that the stabilization of CSS depends markedly on the pore size, on the framework aluminum content and on the nature of the extraframework cation [3]. However, currently all the energetic and dynamic reasons for the long-lived charge separation are not yet well understood and are still under investigations. Among the energetic factors, the knowledge of the activation energy is of high importance because it can help to show the correlation between the electron transfer rate and the free energy by demonstrating a Marcus type dependence for such mechanisms. In that context, we demonstrated previously by studying the effect of the aluminium content on the recombination mechanism that the recombination kinetics in sodium exchanged MFI zeolites doesn’t depend on the activation energy [2]. These experiments showed indeed that the stabilization of photoejected electron and radical cation depends only on the average distance between aluminum atoms.

In the present work, we report the experimental determination of local redox potential in zeolites after the study of a radical cation-electron or radical anion-hole recombination after photoionization of probe molecule incorporated in the internal volume of various channel-type zeolites. With the use of DPH we have been able to determine the redox potential of Zeo/Zeo-• with can explain partially the property of stabilizing electron in zeolite. By the use of electron acceptor (DCB), we demonstrate the ability of the zeolite to eject an electron and stabilizing an electronic hole in the materials and we determine the redox potential of Zeo+•/Zeo by using Marcus theory.

1201 - INSIGHTS INTO LEWIS ACIDIC NATURE OF EXTRA FRAMEWORK ALUMINUM CENTERS INCORPORATED IN ZEOLITES BY ION EXCHANGE

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The catalytic activity of zeolites originates from Brønsted acid and Lewis acid sites. The structure of Brønsted acid sites is well-defined as it stems from a hydroxyl group, which bridges the framework silicon and aluminum atoms of the zeolite [1, 2]. However, due to their plural nature, the structure of Lewis acid sites remains much less defined and sound correlations among the structure of the Lewis acid sites, their amount, and catalytic performance are still missing [1].

In this work, we modulate the Lewis acidity of zeolites, with the aim to understand their structure by quantitatively determining their structure-activity relation. We introduce Lewis acidity into zeolite Y (Si/Al=30) by a facile ion-exchange procedure using aluminum nitrate solution, followed by calcination [3]. The zeolite framework remains preserved after incorporation of extra-framework aluminum, as indicated by X-ray diffraction and N2 physisorption. The introduction of extra-framework aluminum correlated to the number of Lewis acid sites, as illustrated by FTIR spectroscopy of adsorbed pyridine and carbon monoxide. However, no considerable change in the number of Brønsted acid sites was observed. The quantitative analysis of different aluminum coordinations by 27Al MAS and 27Al MQMAS NMR spectroscopies confirms the appearance of a broad asymmetric resonance at ~3 ppm in modified zeolites, which is ascribed to the incorporated extra-framework aluminum species exhibiting octahedral coordination.

The catalytic acitivity of Lewis acid sites introduced in aluminum exchanged zeolites was determined by performing Meervein-Pondorf-Verley (MPV) reduction of 4-tert butyl cyclohexanone using isopropanol as sacrificial alcohol. After ion-exchange, there was a significant improvement in the catalytic conversion and rate of MPV reduction over zeolite catalysts. The catalytic activity of the modified zeolites quantitatively correlated with the concentration of the introduced extra-framework aluminum species and the total Lewis acidity determined by pyridine-FTIR. Therefore, it is inferred that the newly introduced extra-framework aluminum species, which adopt mostly an octahedral coordination under the conditions of NMR measurement, are Lewis acidic and are responsible for enhanced catalytic activity of the aluminum exchanged zeolites [3]. The preservation of Brønsted acid sites further identifies these extra-framework aluminum species as charge neutral, likely in the form of nano-sized Al(OH)3(H2O)3 or Al2O3 clusters [3-5]. The strength and thermal stability of these Lewis acid sites also lead to the improved activity of the modified zeolites in dehydrogenation of light alkanes to light olefins. These results are a significant development towards understanding the nature and role of Lewis acid sites in zeolite based catalysis.

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1249 - STRATEGY FOR STRUCTURAL ANALYSIS OF DISORDER WITHIN THE ALPO4 LTA FRAMEWORK

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Heat storage and reallocation is increasingly important in modern day society. This is where hydrophilic porous solids come into play, having the right properties, that enables them for potential use in technological solutions. One of such materials is microporous LTA aluminophosphate, which achieves heat storage through a process of water sorption. More precisely, the material stores energy in its dry state and releases it during hydration.

To control the course of materials development, we require deep understanding how the process of water adsorption works at the atomic level and for this we need an accurate description of the atomic structure. For crystalline materials this is usually not an issue, since crystallography offers essential information about the average atomic structure needed to explain the macroscopic properties. On the other hand solids can build structures where conventional crystallographic tools fall short. Such examples are amorphous solids, disordered crystals, nanoparticles, solids with various types of defects, materials with adsorbed molecules, crystals with short-range structural fluctuations, etc. In the latter cases we run into trouble, because crystallography suddenly becomes lacking in determination of atomic structure at the nanoscale – we simply phrase this as “the nanostructure problem” [1]. Among these structurally pestilent solids we often find various porous materials because of their complex atomic structures. Their typically large unit cell dimensions, containing several hundred atoms, additionally makes computer simulations and experimental data fits immensely challenging or even impossible.

The whole ordeal seems even dimmer when considering that often different types of materials need different strategies to uncover their atomic nanostructure, consequently making a general strategy impossible. However, comparison of investigated structures with similar known systems can help us immensely in gaining extra information. In our case a well ordered microporous AlPO4-34 [3] was used to help determine some of the limitations of the unknown structure of hydrated AlPO4-LTA.

In this segment a strategy for structural analysis will be presented on an example of microporous aluminophosphate with LTA topology. Water adsorption into its pores makes an otherwise crystalline framework in its dry state highly disordered, while preserving chemical bonding between Al, P and O atoms [2]. Main methods used were X-ray powder diffraction, water uptake measurements, solid state NMR, X-ray and neutron pair distribution function analysis and computer simulations.

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1255 - STRUCTURAL ASPECTS AFFECTING PHASE SELECTION IN INORGANIC ZEOLITE SYNTHESIS

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Discovered by our group in 2014, Hydrated Silicate Ionic Liquids (HSIL) present the long sought paradigm shift enabling the next leap in fundamental zeolite research [1], especially for aluminosilicate zeolites. HSIL are ultra-concentrated, homogeneous alkali-silicate liquids. They consist of soluble, low-nuclear silicate oligomers ion-paired or 'dressed' with partially hydrated alkali cations, reminiscent of silicate melts. The water content per cation does not exceed the first hydration shell of the cations (i.e., not more than a few H2O molecules per cation), and as such, water doesn't function as a true solvent. These liquids are optically transparent, homogeneous, and absent of aggregate or colloidal phases. Doped with aluminum, with care taken not to exceed the aluminosilicate concentration promoting aggregation, these liquids readily yield high-quality zeolites, even at low temperatures and short crystallization times. They offer an elegant synthesis pathway for zeolites, starting from crystallization media absent of heterogeneous phases and concentration gradients, allowing to globally and in situ observe all processes that also happen locally in the interstitial volumes of aluminosilicate gel synthesis systems. In contrast with classical gel syntheses, in HSIL synthesis media the only solid product observed over time is the crystalline zeolite phase, facilitating in-situ measurement and dramatically improving signal-to-noise. HSIL zeolite synthesis has demonstrated that zeolite crystallization and phase selection are no exception to other inorganic crystallization phenomena, but rather adhere to logical and established kinetic, thermodynamic, and physiochemical principles. Concepts like solubility to describe solid-liquid equilibrium and phase behavior, largely ignored in most zeolite studies, are reinstated.

Initially, a large compositional screening study was performed via development of ternary diagrams (Figure 1) [2]. Thus far, HSIL synthesis media allowed to successfully crystallize 16 framework topologies with high quality and purity. In all these syntheses, the aluminum content and corresponding phase behavior of the crystalline products shows a direct correlation to the speciation in the liquid state, as quantified via liquid-state investigation. Predominant parameters determining the speciation include dilution, cation type and temperature. These results show that the framework Si/Al ratio is a thermodynamic parameter, related to the composition of the supernatant solution via solubility considerations, which define the equilibrium distribution of aluminosilicate between liquid and solid fractions (Figure 2).

Evaluation of the crystal structure and distribution of extra-framework cations in all obtained frameworks enabled to formulate a coherent and widely applicable selection criterion for zeolite phases in inorganic synthesis systems [3], describing the relation between the observed framework Si/Al ratio and resulting topology: For a given framework Si/Al ratio, the crystal energy is minimized by crystallizing in the topology yielding the lowest number of vacant cation positions. The criterion is based on the tendency of the crystal to strive for maximum stability by optimizing mutual interactions between framework oxygen and alkali cations (Figure 2). This readily explains sharp phase boundaries in crystallization diagrams, ubiquitously observed in inorganic synthesis, and resolves the mystery of why a single alkali cation may template a multitude of topologies in similar crystallization media.

1294 - QUANTITATIVE LOCATING TITANIUM IN THE FRAMEWORK OF TITANIUM SILICALITE 1 BY EXPLOITING ANOMALOUS X RAY POWDER DIFFRACTION AT THE TI ABSORPTION K EDGE

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Titanium silicalite-1 (TS-1) is a well-recognized and industrially utilized zeolite-type catalyst active in several partial oxidation reactions. It stays of particular interest for olefin epoxidation process with aqueous H2O2 as oxidant since it releases only water as a byproduct. It owns its unique performance to tetrahedrally coordinated titanium that replaces silicon in its MFI type framework structure and acts as a catalytically active site in formation of peroxo-species. The location and vicinity of titanium positions in the TS-1 framework structure defines not only the accessibility and geometry of active sites, but also the nature of the mechanism that controls the reaction. Up to date it remains disputed whether the peroxo-species form on titanium monomers, within bridged di-titanium sites, or within clusters of higher nuclearity [1,2]. Although a number of diffraction and spectroscopic techniques have been applied to solve this problem, no clear picture of the nature of the Ti site(s) in TS-1 has emerged. The ambiguous assignment of Ti positions is hindered by the fact that the titanium

concertation in the framework is low and the substitution for silicon on a T-site can be only partial. To pinpoint titanium to specific T-sites in TS-1 framework we have used anomalous X-ray powder diffraction (AXRD) at the Ti absorption edge (4.96 keV). In this way, the titanium positions in the structure were identified by exploiting the drastic changes in titanium X-ray scattering factor. While at X-ray energies far from the absorption K-edge, the X-ray scattering power of titanium is a primary function of the number of electrons, at energies close to the absorption edge, it dramatically changes by the anomalous contributions to the X-ray scattering factor of the element. Thereby the signal scattered by TS-1 lattice decreases for titanium positions while for silicon positions it remained unchanged. This change consequently affects the structure factors and the intensities of the corresponding Bragg reflections. Overall, the difference between the off- and on-resonance structure factors allowed the titanium positions in the structure to be quantitatively determined. Using this approach, two TS-1 samples of similar chemical composition Si(96-x)TixO192, where x~2.5, but which were synthesized under different conditions, were examined. The refinement of the first structure confirmed the previous studies [1] on the large contribution from higher coordination and non-framework titanium in that sample. Within a unit cell of the second structure, 0.6 and 0.5 titanium atoms were found concentrated at sites T3 and T9 of MFI-type framework, respectively. Remaining titanium atoms are disordered over several sites. Overall titanium concentration converged to 2.6 Ti atom per unit cell. Titanium atom sitting at T3 site appears as an isolated species. One at T9 could exist as di-nuclear site, however such configuration is less probable.

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1309 - WATER STRUCTURE IN SILICA MESOPORES EFFECT OF PORE WALL POLARITY

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Hydrogen bonding between water molecules is restricted in the spatial constriction of cylindrical silica mesopores. In addition to the pore size, the pore wall also affects how water behaves due to the strength of interactions with water molecules [1,2]. The degree of interactions at the solid-fluid interface determines the molecular orientation and coordination, i.e., the 'structure of water'. The pore wall-to-water interactions can be chemically tailored by altering the silica surface. The silanol group (Si-OH) density of the pristine (hydrophilic) mesoporous silica used in this study is about 2 nm-2 at a pore size of less than 4 nm. About 80% of these groups undergo a reaction with trimethylsilyl chloride and are subsequently transformed to ≡Si-O-Si(CH3)3, which leads to a hydrophobization of the pore´s surface.

The results from N2 and H2O sorption experiments are combined, revealing the degree of functionalization and the surface chemistry of the silica pores. The chemical changes on the surface lead to changes in polarity that directly affects the structure of water within the porous host drastically. The silica materials with hydrophilic and hydrophobic pore walls are loaded with water, followed by IR spectroscopy investigations of the water bands in the region of 4000-2800 cm-1. The hydrophobic environment leads to surface-near water with a coordination number of ~4.0 which resembles 'ice-like' water that exhibits fewer degrees of freedom than 'liquid-like' water with a coordination number closer to 4.4. The latter can be observed more towards the center of the hydrophilic pore but dominates within the hydrophobic environment. The poor wall-to-water interactions can explain these observations after chemical hydrophobization of the silica surface.

Computational data support the experimental observations. Calculating the coordination number, surface distance, and angular distribution of water relative to the silica surface led to a more profound understanding of the interactions at the solid-fluid interface. The water molecules show a wide distribution of angles relative to the surface, as one would expect in non-confined water when located in the hydrophilic pore. However, in the hydrophobic pore, the angle distribution is smaller because of the less-favourable interactions of the water with the pore surface. As a result, water is more likely to point toward the surface with both hydrogen atoms than with only one hydrogen or oxygen in both environments.

Simulated sum-frequency generation (SFG) spectra deliver surface-specific information about the orientation of water stretching modes and complement the experimental results. The combination of experimental and theoretical results enables profound insight into the interplay between mesopore surface polarity and water structure within a confined environment of silica pores. [3]

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1334 - XANES ANALYSIS OF TRIMETAL CU MN FE POROUS SILICA SUPPORTED CATALYSTS FOR FOTO FENTON LIKE WASTEWATER TREATMENT

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Pollution of surface water by organic contaminants of emerging concern (CEC) has become a serious problem in recent decades. To degrade CEC to inorganic compounds, various systems of advanced oxidation processes (AOPs) have been intensively studied. In the classical Fenton reaction, iron salts (Fenton reagent) are used as catalysts in the presence of hydrogen peroxide (oxidant) [1]. The application of the Fenton process (homogeneous catalysis) is limited mainly for three reasons: (i) narrow acidic working conditions (the optimum pH is 2.8–3.5), (ii) the generation of large amounts of iron sludge, and (iii) the need for post-treatment of effluents containing excess iron ions to ensure the regulated water quality levels. To overcome these limitations, Fenton-like reaction at neutral pH using a heterogeneous catalytic system is the method of choice. We have prepared trimetallic Cu-Mn-Fe catalysts on porous silica supports and tested them for Fenton-like and photo-Fenton-like degradation of bisphenol A and coumarin as model CEC. The method of immobilisation of the transition metals on and/or in the silica structure is crucial, since the surface area and functionality of the porous silica determine the nature and distribution of the metal cations and thus their catalytic activity [2]. We used different characterization methods (XRD, EDAX, TEM, Raman and UV-Vis) to determine the structural properties of the catalysts. To precisely determine the nature of the metallic centres, we performed Mn, Fe and Cu K-edge XANES (X-ray absorption near edge structure) analysis to quantify the valence state and local symmetry of all three metal sites [3]. Isolated Mn cations incorporated into the porous silica support contribute to Fenton-like catalytic activities at near-natural pH. The photo-Fenton-like activities were attributed to the Mn and Cu components acting as semiconductors and harvesting visible light. Moreover, the CuO nanoparticles attached to the porous silica support stabilized the Mn leaching into the liquid phase. Fe oxide nanoparticles covered with the silica support do not contribute to the catalytic performance, but have magnetic properties, resulting from the different occupation of the tetrahedral and octahedral sites. The magnetic properties of Fe allow easy separation of the catalyst from the treated wastewater after the catalytic reaction, making the catalysts even more applicable.

POSTER ABSTRACTS

CATEGORY: ADVANCED SYNTHESIS (ZEOLITES, ZEOLITE-LIKE MATERIALS, MOFS, OTHER POROUS SOLIDS)

1021 - PHOTOCATALYTIC ACTIVITY OF CLINOPTILOLITE RICH ZEOLITIC TUFFS FROM DIFFERENT REGIONS

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Due to their unique structural properties, low cost and environmental compatibility, natural zeolites have been recognized as effective supports for photocatalytic particles such as transition metal oxides (e.g. TiO2, NiO, ZnO, CuO, SnO2, Fe2O3) in the catalytic degradation of complex organic dyes present in water media [1, 2]. The lattice of zeolite prevents the aggregation of oxide species but also contributes to the electron-hole recombination. It has been noticed that pure clinoptilolite (CLI) exhibits a photocatalytic activity in the degradation of rhodamine B. This is explained by the presence of Ti and/or Fe species, which are usually impurities in zeolitic tuffs [3]. The present study focuses on CLI-rich natural zeolitic tuffs and their photocatalytic activity in the degradation of cationic organic dyes such as methylene blue (MB). CLI from different regions and deposists was tested: a) Serbia – Slanci (SCLI), b) Turkey – Gördes (TCLI), c) Iran – Semnam (ICLI), d) Romania – Baia Mare (RCLI) and e) Slovakia – Nižný Hrabovec (SKCLI). Samples were sieved to obtain the particles with the size in the range 63 and 125 µm mesh, washed with deionized water, dried at 105 °C overnight and tested without any additional treatments. Photodegradation tests were performed using a batch reactor system equipped with a 50 cm3 Pyrex glass cell and by a circulating water jacket to keep the constant temperature at 25 °C. All tests were done at atmospheric pressure. Suspension contained water solution of MB (C0= 10 mg dm–3) and photocatalyst in the concentration of 0.2 g dm–3 at different pH (pH= 3, 6, or 9), was continuously stirred by magnetic stirrer for 30 min to achieved an adsorption/desorption equilibrium and then irradiated for 300 min. Osram Ultra Vitalux lamp (300 W) served as visible light source, positioned 10 cm above the photocatalytic reactor. The concentration of MB was measured colorimetrically at λ= 664 nm by using an UV/VIS spectrometer.

The obtained results showed that the overall degradation of MB by the photocatalytic process can be attributed to the joint effect of initial adsorption and degradation under visible light irradiation. The adsorption amounts indicated that CLI has two roles: adsorption of MB during the dark phase and photocatalytical. The adsorption increased with pH. The photocatalytic degradation is also affected by pH showing the best activity for all studied zeolitic tuffs at pH= 6. The rate of MB degradation varied from about 36-47% while the total degradation was 70-91%. The photocatalytic activity was attributed to the presence of Fe species showing a linear increase with the Fe content in the tuffs. The MB photodegradation follows the Langmuir–Hinshelwood kinetic model. The recyclability tests showed that the degradation rate decreased from 91 to 69% during three reaction cycles, demonstrating a promising potential of CLI in the treatment of textile industry wastewaters.

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1037 - SOLVENT ASSISTED LIGAND EXCHANGE OF ZIF 4 FOR GLASS PREPARATION

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With the current increasing interest in MOFs and ZIF glasses for a variety of applications, optimal and environmentally friendly synthesis of the materials to be vitrified is essential. A comprehensive research has been done so far on the thermal behaviour and structure of ZIF-4 (Zn(imidazolate)2). It exhibits several solid-liquid-solid transitions and a melting (Tm) and decomposition temperature (Td) of 593 and 602 °C, respectively.[1] However, because of the high Tm value, oxidation can occur during melting, resulting in ZnO contamination. A mixed-ligand version of ZIF-4 can be prepared using benzimidazole (bIm), resulting in the compound ZIF-62 [Zn (Im)2-x(bIm)x], which has the same framework topology as ZIF-4. The partial ligand replacement lowers the Tm value to 435 °C, resulting in a more stable liquid state.[2]

Here we present a post-synthesis modification of ZIF-4 via Solvent Assisted Ligand Exchange (SALE) with benzimidazole, as well as the resulting amorphous glasses. SALE was performed in methanol for three days at 60 °C using prepared ZIF-4 crystals. The SALE-ZIF-4 was first activated by soaking in methanol, followed by vacuum heating, and then analysed using digestion liquid 1H NMR to determine the bIm/Im ratio. The ratio was determined to be 1 bIm to 5 Im, as opposed to ZIF-62's ratio of 1 bIm to 7 Im. The activated SALE-ZIF-4 was pelletized, then heated to 350 °C and naturally cooled to 200 °C then quenched to room temperature to produce amorphous glass denoted as agSALE-ZIF-4.

The experimental powder X-ray diffraction patterns of crystalline SALE-4 are in good agreement with the calculated diffraction pattern of ZIF-62, however a slight peak formation at 2θ ~ 7° is present, indicating the presence of possible ZIF-7 impurities. The PXRD pattern after vitrification shows a broad peak at 2θ ~ 15°-, demonstrating the collapse of crystalline structure and the material's amorphous nature. SEM analysis was performed on both crystalline and glassy samples, and the glassy sample clearly showed melting as well as porosity with some cracks present, which could be the result of quenching. Both the crystalline and the glassy sample were also characterized using N2 physisorption, MAS-NMR, TGA/DTG and DSC.

In conclusion, we successfully applied a SALE approach for a post-synthetic modification of ZIF-4 and produced the final amorphous glass, termed as agSALE-ZIF-4, that was transparent and, most importantly, bubble-free.

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1048 - TETRAHEDRAL PB(II) METAL ORGANIC FRAMEWORK SYNTHESIS CHARACTERIZATION AND ADSORPTION PROPERTIES

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Microporous crystalline MOFs (Metal-Organic Frameworks) are formed by the self-assembly of inorganic metal clusters and organic linkers. Both inorganic (metal clusters) and organic (ligands) constituents of MOFs can be varied in their shape, size, composition, geometry, and branching modality. This allows tuning the structure and properties of MOFs to produce a versatile class of porous crystalline solids with a wide range of properties, high porosity, and surface area. Excellent examples of polytopic ligands with great potential to serve as building blocks in MOFs construction are bulky tetrahedral linkers. As a continuation of our research, in the present work, we focused on

the synthesis of novel MOFs using a rigid tetratopic ligand derived from methanetetrayltetrakis(benzene-4,1diyl)tetrakis(aza))tetrakis(methan-1-yl-1-yliden)tetrabenzoic acid, H4MTA [1].

The aim of the work is focused on the synthesis of tetrahedral tetraazo-tetracarboxylic acid (H4MTA) which was prepared by the multistep organic synthesis according to the described procedure [1]. A solvothermal reaction between H4MTA and $Pb(NO3)2·5H2O$ in a $DMF/H2O$ mixture afforded orange needle-shaped single crystals of $\{[Pb2(MTA)(H2O)3]·H2O·4DMF\}n$ (UPJS-18). These formulae were established based on the single-crystal X-ray diffraction (SC-XRD) experiments, elemental analyses, thermogravimetric analysis (TG), and infrared spectroscopy (IR). Thermal stability and activation condition of the materials were studied by the combination of in-situ heating DRIFT and TG. Activated compounds were further tested as gas adsorbents for nitrogen, argon, carbon dioxide, and hydrogen, with a combination of high-pressure adsorption measurements for H2 and CO2. The SC-XRD analysis reveals that UPJS-18 crystallizes in the tetragonal space group I-4. All carboxylic groups of the H4MTA molecule are deprotonated and coordinated to the central atoms in chelate-anti mode. One MTA ion coordinates to eight lead central atoms. The coordination sphere of each central atom is completed by three coordinated water molecules where two of them make a bridge between two lead metal ions. By bridging the carboxylate and aqua ligands, the central atoms are arranged in 2D linear chains propagating along a and c crystallographic axis, with the sizes of channel apertures are 10.70 × 10.72 Å2 (c-cryst. axis) and 18.07 × 17.94 Å2 (a-cryst. axis). Infrared spectroscopy confirmed the presence of water in the framework system and MTA4- ligand In-situ heating DRIFT analysis with a combination of TG showed, that porous complex undergoes to desolvation process after heating to 350°C and dehydrated form of UPJS-18 is than highly thermally stable up to 380°C. The activated porous complex was subjected to adsorption measurements of various gases which showed that the compound can be used as an effective adsorbent in the separation of CO2 from N2. UPJS-18 adsorbs only a limited amount of N2 at -196°C or Ar at -186°C but surprisingly compound adsorbs CO2 at 0°C with a maximal storage capacity of 31 cm3 g-1 corresponding to 6.1 wt.% (23 cm3 g-1 corresponding to 4.2 wt.% for 20°C). UPJS-18 was also subjected to high-pressure adsorption of CO2 and H2 at various temperatures. Detailed results will be presented at the conference.

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1058 - NH3 SCR CATALYSTS FOR HEAVY DUTY DIESEL VEHICLES PREPARATION OF CHA TYPE ZEOLITES WITH LOW COST TEMPLATES

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Recent regulations are forcing the development of efficient NH3-SCR catalysts for heavy-duty diesel vehicles, i. e. trucks. These heavy-duty diesel applications present lower temperature requirements for their exhaust treatment systems, and, in addition, require much larger catalyst volumes compared to light-duty diesel vehicles. For this reason, less cost-intensive Al-rich zeolite preparation procedures have become a clear target trying to fulfil the future needs of the automotive industry. In fact, Cu-containing Al- rich small pore CHA zeolites with Si/Al- 4-6 show enhanced low-temperature SCR activity compared to their high-silica counterparts [1-3].

Herein, we describe a computer-aided methodology to select the most adequate low-cost OSDA molecules to maximize the Al-rich CHA zeolite crystallization. In a first step, a DFT study has been carried out to evaluate the ability of slightly different simple and commercially available alkylammonium cations to stabilize the CHA structure, where these alkylammonium cations are tetraethylammonium (TEA), methyltriethylammonium (MTEA) and dimethyldiethylammonium (DMDEA). Remarkably better stabilization energies are obtained for MTEA.

Then, the synthesis of Al-rich CHA-type zeolites has been attempted using TEA, MTEA and DMDEA. In agreement with the theorical information, both TEA and MTEA allow the crystallization of CHA, but TEA produce less pure crystals with a stacking intergrowth, formed by large domains of CHA with narrow faulted GME domains that allow the presence of larger cavities than cha cages, as revealed by electron diffraction and high-resolution transmission electron microscopy.

Both CHA-type materials, have been exchanged with copper and their catalytic performance for the NH3-SCR reaction has been evaluated under fresh and hydrothermal ageing conditions relevant for future heavy-duty diesel conditions. These two materials exhibit similar and excellent catalytic activity and hydrothermal stability, unaffected by the presence of sodium cations or the presence of stacking intergrowths in the samples synthesized using TEA as OSDA [4].

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1061 - CO BASED MOFS FOR BIOMASS DERIVED MOLECULES UPGRADING

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Due to continuous depletion of non-renewable fossil fuels deposits and subsequently, increasing levels of greenhouse gases, industry must employ greener and more sustainable feedstocks, such as biomass, for the production of value-added products. From the large spectrum of molecules that can be obtained from biomass, the furanic compounds and carboxylic acids are useful feedstocks for the production of fine chemicals, fuel-additives and biofuels [1,2]. 5-Hydroxymethyl-2-furancarboxylic acid (HMFCA), for instance, is obtained from the partial oxidation of 5-hydromethylfurfural (HMF) and is an important building block for both polymer and pharmaceutical industries [3]. However, only a few studies focus on the targeted production of HMFCA by applying stoichiometric, catalytic or biocatalytic oxidation, each of these approaches having some drawbacks but the same major challenge, namely the easy over-oxidation towards the dicarboxylic acid [4]. Besides oxidation, hydrogenation of biomass feedstock is also intensively studied. Hydrogenation of levulinic (LA) and succinic (SA) acids yields to lactones which are used as solvents and fuel-additives while further hydrogenation produces their corresponding alcohols which are employed by polymer industry [5,6]. Regardless of the valorisation pathway, heterogeneous catalysis is preferred as it brings many advantages, such as easy recovery, recyclability and possibly more sustainable reaction conditions.

Metal-organic frameworks (MOFs) are a class of hybrid organic-inorganic materials, renowned for their structural properties, particularly their tunability and easy design [7], which makes them good candidates as advanced materials for gas storage as well as catalysis. Since their discovery, MOFs have known a continuous growth and interest, with a large number and diversity of structures existing nowadays, many of which embrace the water- and thermal stability. Thus, expanding the MOFs application, especially in biomass upgrading processes as promising alternatives to classic solid catalysts is expected [8].

In this context, the aim of the present study was to develop Co-based MOFs catalysts able to combine a high catalytic efficiency with a high hydrothermal stability in upgrading of renewable HMF towards HMFCA and LA and SA to their corresponding diols, respectively.

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1069 - MANIPULATION OF SYNTHESIS FOR STABILIZING THE STRUCTURE VIA CRYSTAL ENGINEERING OF SYNERGISTIC COMBINATION AN EXAMPLE OF NIOBIUM SILICATE

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Microporous silicates have been widely used as catalysts and adsorbents. The synthesis of silicates with transition metals broadens the field and scope of applications. Much work have been done on silicates with stoichiometric amount of titanium, zirconium and vanadium. However, only a few studies were done for the other systems. Microporous niobium silicates are one of the few systems which are not well studied. Rb2(Nb2O4)(Si2O6)·H2O was synthesized via a high-temperature (600 ºC), high-pressure hydrothermal reaction in 2008 [1]. Its structure possesses perpendicular connected corner-sharing -Nb-O-Nb-O- octahedra chains which are further connected by square rings of silica tetrahedra Si4O12, resulting in a three dimensional framework structure with 2D 8-ring channels. No further study of this material is found since then. Considering its high temperature hydrothermal synthesis condition and expensive Rb resource limits its application explore, the new synthesis strategy and procedure are required.

The fully replacement of Rb by Na was reported here. Since Na is much smaller than Rb, in order to stabilize the framework by Na, more cation may be required in channels. To compensate the extra positive charge from cations, the charge of metals in framework need be reduced, which could be achieved by replacing Nb5+ by M4+ or M3+ with similar ionic size. Furthermore, those metal ions need have ability to form corner-sharing octahedral chain. In this work Fe3+, Ti3+ and V3+ were selected to prove this concept and the syntheses were done statically at 230ºC under autogenous pressure. With this strategy, the Fe-, Ti- and V- substituted microporous sodium niobium silicate with the Rb2(Nb2O4)(Si2O6)·H2O structure were successfully synthesized. The syntheses have been optimized and shown to be very sensitive to the composition of the precursor gel, especially the content of Fe, Ti and V. Samples of good phase purity could only be obtained in the presence of fluoride ions in starting gel, which, however, did not end up in the final solid. Their structures have been confirmed by powder x-ray diffraction. The materials have further characterized by scanning electron microscopy, energy dispersive X-ray spectrometry, solid state nuclear magnetic resonance, thermogravimetry analysis and Raman spectroscopy. The Fe substituted material showed the ability to remove Rare-Earth Elements from water [2]. Since Fe and Na are much cheaper than Nb and Rb, and the synthesis temperature is 230 ºC, the result of this work may promote the research of its application.

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1076 - BEYOND TIN CONTAINING ZEOLITES – NOVEL HETEROGENEOUS POROUS TIN ORGANIC FRAMEWORKS FOR THE CATALYTIC CONVERSION OF KETONES

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The Meerwein-Ponndorf-Verley (MPV) reaction is a highly chemoselective reduction of aldehydes and ketones to alcohols. It proceeds via a 6-member ring transitioning state in which the aldehyde or ketone as well as a secondary alcohol coordinate to a Lewis acid metal center, resulting in a hydride transfer from the alcohol to the ketone [1]. The reverse reaction in the occurring equilibrium is the Oppenauer oxidation. This system (MPVO) can be used to modify platform chemicals. Generally, the MPV is catalysed homogeneously, but several heterogeneous catalysts have been developed with similarly high activities and selectivities. Corma et al. utilized a tin-beta zeolite catalyst, reaching up to 91% conversion of cyclohexanone, with 100% selectivity to cyclohexanol. Isopropyl alcohol was used as a solvent as well as reactant [1].

Tin-beta zeolites are well established catalysts used in a variety of reactions, due to their Lewis acid tin-centers. Inspired by this type of material, novel porous organic frameworks (OF) bearing covalently bound Lewis acidic sites (Sn-OFs, Sn-HCP) were developed for the isomerisation of aldoses [2]. Contrary to expectations, Sn-OFs and Sn-HCP exhibit unique catalytic activity for selective epimerization of monosaccharides at position C2 instead [2]. Both Catalysts were utilized for the MPV reduction of cyclohexanone, reaching up to 36% in conversion, with 100% selectivity to cyclohexanol. This similarity to the tin-beta zeolite suggests the same mechanism for the occurring hydride transfer [1].

The Sn-OFs are synthesized according to the organolithium route via a nucleophilic aryl lithium intermediate which is cross-linked by a tin-based precursor under formation of an Sn-C bond [3]. The tin-attached hydroxyl groups are suggested as catalytically active sites, which are formed due to partial hydrolysis during the synthesis and work-up procedure [2]. The synthesis procedure of the Sn-HCPs is based on a Friedel-Crafts alkylation via a metal-free direct external crosslinking of the tin-organic monomers. Contrary to the Sn-OFs, the active sites of the Sn-HCPs based on a crosslinking route [4] are not introduced due to structural defects, which results in well-dispersed active sites.

The obtained materials exhibit permanent porosity with specific surface areas up to 500 and 1300 m2 g-1 for Sn OFs and Sn-HCPs, respectively. The catalysts were characterized by FTIR, 1H, 13C, and 119Sn MAS NMR, dynamic nuclear polarization (DNP) 119Sn MAS NMR [6], XAS, and TG-DSC. The results confirm the formation of a highly hydrophobic material with confined pore spaces with partially hydrolysed Sn-sites [5].

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1078 - STRATEGIES TO CONTROL THE AL DISTRIBUTION IN ZEOLITES THERMODYNAMIC AND KINETIC ASPECTS

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The performance of zeolites is related to the density, strength, and location of intrazeolitic active sites. Brønsted acid sites in zeolites, acting as the active site in acid-catalyzed reactions, are generally created when protons compensate for the negative framework charges induced by incorporating Al3+ into a silica framework. It is thus not difficult to see that the position and relative concentration of Al atoms in the tetrahedral sites (T-sites) of the framework can alter the location and properties of acid sites in zeolites. Furthermore, the distribution of proximal Al sites can generate exchangeable sites to stabilize multivalent extra-framework species. Apart from its effect on the formation of active sites for redox catalysts, the proximity of Al sites in the framework has been demonstrated to influence the selectivity in acid-catalyzed reactions, giving very different results from materials with nearly equal amounts of framework Al content [1-4]. Therefore, considerable attention has been devoted to controlling the Al incorporation to optimize the performance as industrial solid catalysts and to develop new acid- and redox-catalyzed reactions.

Here we review direct bottom-up synthetic strategies with the aim of addressing and analyzing the impact of thermodynamic vs. kinetic contributions on the Al incorporation in zeolites. A glance at all these synthetic strategies reveals that the unique arrangement of Al atoms in zeolites can be feasible by (i) controlling or aiming toward the energetically preferential Al sites and (ii) forming specific (alumino)silicate networks and controlling their reactivity and/or dissolution rates. Energetically preferential Al siting at desired locations in the zeolite framework could be induced by creating new geometric and/or electrostatic interactions between negatively charged framework units and SDAs. In addition, the second heteroatom has a thermodynamic preference for a particular T-site due to its different average T-O distance and T-O-T angle from Si (or Al), which could be exploited in competition for Al incorporation. Specific (alumino)silicate networks could be formed through in-situ methods by changing the Si and Al sources and the mixing order of zeolite ingredients, as well as ex-situ methods using preformed amorphous and crystalline precursors. Controlled (alumino)silicate networks are thought to have different dissolution behaviours that influence the properties of the dissolved (or re-organized) (alumino)silicate species in the liquid phase. The formation of anomalous Al-rich zones in the synthesis mixture before or during the hydrothermal treatment may be one of the important factors for obtaining zeolites containing proximate Al sites. Especially, the distribution of proximal Al sites in some resulting zeolites was kinetically controllable depending on the pre-dissolution time of the (alumino)silicate precursors and/or additional crystallization time after obtaining a fully crystalline final product. Although the generic interpretation of each strategy and underlying crystallization mechanism remains largely unknown (and often limited to a specific framework), this review will provide guidance on more efficient methods to prepare fine-tuned zeolites with desired chemical properties [5].

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1089 - HYDROCRACKING OF FISHER TROPSCH WAX OVER PT BEA NANOSHEETS

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Hydrocracking of Fisher-Tropsch wax into middle distillates maximises the diesel yield and improves its cold flow properties by hydroisomerisation. In this process bifunctional catalysts, composed of the metal function which provides (de)hydrogenation and the solid acid support which provides cracking and isomerisation, are used.[1]

Zeolites are preferred over amorphous solid acid support because of their high thermal and hydrothermal stability, which is a result of their crystalline morphology. However, bulky molecules are restricted from accessing internal acid sites where there is high internal surface area due to their small pores. These diffusion limitations also cause slow internal mass transfer of products to and from the active sites which might lead to secondary cracking of the intermediates into the gaseous products and cause coke formation which could block the pores and cause catalysts deactivation.[1, 2]

Zeolites with a hierarchy of pores (micropores and mesopores) have been introduced to overcome the diffusion limitations while maintaining stable crystalline morphology. Top-down desilication and dealumination methods, and bottom-up hard and soft templating methods are used to generate mesopores. There is no control on the mesopore generation through the top-down methods which might lead to the formation of an amorphous solid support which is less stable. Uniform mesopores are generated via soft templating method through the use of structure directing agents.[3]

The cationic quaternary ammonium surfactants with dual porogen function are used as structure directing agents for the synthesis of zeolite nanosheets.[4] During crystallisation, the hydrophilic ammonium groups direct the micropores generation while the hydrophobic alkyl tails direct the mesopores, producing 2D nanosheets. In this study cationic surfactants with varied tail lengths will be used to synthesise BEA nanosheets to study the effect on the mesopore diameter and whether nanosheets will be stacked randomly or in multi-layered form. Pt will be loaded using wet impregnation and hydrocracking performance will be studied. The following characterisation techniques will be used: solid-state NMR, XRD, FTIR, TEM, STEM, NH3-TPD, N2 physisorption, and CO Chemisorption.

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1096 - OPTIMIZATION OF THE TI INSERTION INTO TITANIUM SILICALITE 1 CATALYST THROUGH THE DESIGN OF EXPERIMENT APPROACH

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Titanium Silicalite-1 (TS-1) [1] is a zeolite used as catalyst in partial oxidation reactions, whose composition is x TiO2 (1-x) SiO2. The active sites are tetrahedral Ti atoms, isomorphously substituted in the MFI framework. The TS-1 catalytic activity is influenced by the Ti coordination, which can spread from tetra- to octahedral, depending on the Ti content and the synthesis procedure. [2] Therefore, a rational screening of the important parameters in the TS-1 synthesis was done, to see which one has a significant effect on the material obtained. [3] The Design of Experiments (DoE) [4] is a powerful tool that can be used to explore the effect of the different synthetic parameters, avoiding the unreliable trial-and-error traditional approach in zeolite synthesis. The screening study [3] allows to exclude the parameters that do not have a significant effect from further studies and focus the attention on the significant ones. Using the information

obtained from the screening design and implementing some precautions adapted from the patented synthesis procedures, an optimization of the TS-1 synthesis will be conducted using the same approach. Particular attention will be paid to the alkaline metals impurities in the reagents and to the purity of the Si and Ti precursors. The investigated synthesis procedure is composed by: (i) separate hydrolysis of the silicon(IV) ethoxide in an aqueous solution of the organic structure directing agent and the titanium(IV) ethoxide in ethanol at low temperature, (ii) mixing of the solutions followed by an aging period and (iii) hydrothermal crystallization. The time of crystallization will be varied between 1 and 3 days, the temperature of crystallization between 150 and 190°C and the Ti/Si molar ratio in the synthesis gel between 0.014 and 0.02. All the other parameters will be kept constant. A D-Optimal Design was planned that allows to determine the linear, quadratic and combination effects of the variables. For all the samples, the total Ti content will be determined by Energy Dispersive X-Rays Spectroscopy and the Ti coordination was determined by means of (i) the vibrational band, fingerprint of the tetrahedrally coordinated Ti atoms, in the MIR spectra [2] and (ii) the Ligand to Metal Charge Transfer electronic transition of Ti, in the UV-Visible spectra, whose wavelength is sensible to the Ti coordination. [2] The multivariate analysis of the samples characterization will finally allow to obtain an optimized TS-1 sample.

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1107 - STRATEGY TO MAXIMIZE AL CONTRIBUTION IN FORM OF AL PAIRS IN ZSM 5 ZEOLITE

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Control of Al organization in silicon-rich zeolite matrices represents an important issue as it governs the catalytic performance of both acid and redox sites and represents one of the key parameters of the zeolite-based catalyst.[1,2] Isolated Al atoms, Al pairs (Al-O-(Si-O)2-Al sequences in one zeolite ring), and close unpaired Al atoms (two close Al atoms located in different rings) were reported for silicon-rich zeolites.[1]
ZSM-5 zeolite represents the most prominent for catalytic applications silicon-rich zeolite. For this reason, synthesizing ZSM-5 materials with a maximized concentration of Al species, providing a high concentration of active sites suitable for selected processes, attracts significant attention. Isolated Al atoms and Al pairs (located in 6-member rings) were reported to be present in this matrix, and significant effort was spent to reaching (semi)monomodal ZSM-5 matrices with prevailing single Al atoms or Al pairs using control of reaction conditions (nature of Al and Si sources, presence of co-cations, etc.).[3,4] However, the preparation of ZSM-5 zeolites with a high fraction of Al pairs was limited to materials/samples with rather higher framework Al content ($Si/Al < 40$).
In this contribution, a new synthesis protocol enabling the preparation of silicon-rich ($Si/Al > 50$) ZSM-5 zeolite matrices with over 80 % of Al atoms in Al pairs is reported. This method is based on the preparation of two gels (all-silica one and Al-rich one), which are aged and subsequently combined together before final crystallization under hydrothermal conditions. In the Al-rich gel, Al-O-Si-O- sequences are formed, and they are preserved after mixing of Al-rich gel with the all-silica one and transferred to the ZSM-5-framework of the resulting material. Al distribution in the zeolite product was analysed by Co(II) ions as a probe, and Al arrangement in gels was monitored by 27Al MAS NMR spectroscopy. The suggested here mechanism of transferring larger Al-O-Si-O-Al sequences into ZSM-5 product can be considered in analogy to the one already proved for SSZ-13 zeolite synthesized using various zeolites as Al and Si sources. [5] The reported synthesis strategy to maximize the concentration of Al pairs in silicon-rich matrices seems to be not limited by the structure directing agent or Si and Al sources used in gel preparation. Thus, it represents a very promising tool for tuning Al distribution in various silicon-rich zeolite matrices.

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1116 - TRICATIONIC 1 4 7 TRIAZACYCLONONANE COBALT COMPLEX AS SDA IN THE SYNTHESIS FOR DIFFERENT ZEOTYPES

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Zeolites have a wide range of application i.e. as molecular sieve or catalysts for organic reactions. In order to design the properties of these materials the pore size and form plays a decisive role which could be controlled by structure-directing agents (SDA). These are typically organic amines or alkylammonium salts. Additionally, it is possible to use metal complexes-use metal complexes. Here, we describe the synthesis with the tricationic [Co(tacn)2]3+ complex (1,4,7-triazacyclononane = tacn) as SDA in a typical hydrothermal synthesis for different zeotypes. By using only silica as precusor a yellow zeotype called LMU-2 (Ludwig-Maximilians University – 2) is obtained.[1] The structure is similar to the chabazite (CHA) but has an interrupted porous framework (–CHA) due to the large complex molecule located in the cages. The crystal structure of the LMU-2 is determined by 3D electron diffraction and the hydrogen atom of the [Si–O···H···O–Si]– hydrogen bond of the interrupted framework, whose position could previously only be calculated by molecular modelling, can be located by using this method.

In addition to pure silica material, germanium, aluminum, boron or a mixture of two of these can also be added during synthesis. The PXRDs of the resulting materials show different reflection pattern. Depending on the reaction condition and heteroatom concentration reflection patterns of LMU-2, CHA or a mixture of both is obtained. The properties, such as color or hydrophobicity, also change and were characterised using different spectroscopic and physisorption methods.

Water physisorption measurements of calcined LMU-2 show that the hydrophobicity can be influenced by using different heteroatoms, which could have a significant impact on its application as a catalyst. Additionally, the color of the material changes during calcination from yellow to blue or pink depending on the added heteroatom. The change of the color show that the coordination of the cobalt changes and that cobalt has been incorporated in the framework in each material. The oxidation state and the coordination of the cobalt is analysed using different spectroscopic methods. Exposure to different gases like NOX changes the color and the coordination of the cobalt. IR spectroscopic measurements show two characteristic bands at 1420 cm–1 and 1323 cm–1 which are also found in IR spectra of Na3Co(NO2)6 complexes. [2] These cobalt containing materials are interesting candidates for various oxidation reactions, like the oxidation of ethanol to acetaldehyde or the oxidation of phenol with peroxymonosulphate.[3,4]

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1119 - INDUSTRIAL MANUFACTURING OF ZEOLITE MOLECULAR SIEVES

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Synthetic zeolite molecular sieves are developed in the mid of the 20th century and are used in industrial applications since more than 60 years, mainly as highly efficient adsorbents for separation or thermo chemical energy storages processes in gas or liquid phase. Zeolite molecular sieves can be applied in powder form, due to the high pressure drop preferably in static applications, but to a much larger extent as shaped material in both static and dynamic (flowing media) applications. Many shaping technologies for molecular sieves like extrusion or granulation were developed over the last decades, reflecting the different requirements for molecular sieves in different applications. This review deals with the influence of the applied shaping methods for hydrophilic zeolite molecular sieves as bulk material as well as for shapes with higher geometrical requirements like honeycombs or multi-channel tubes on the potential industrial applications; thereby considering powders, binder containing shapes as well as binderfree shapes.
The starting material for most of the zeolite molecular sieves is the zeolite powder. The properties of the zeolite powder can be adjusted in the synthesis or in post synthesis processes. Bringing said powder into the by the application process required shapes, suitable shaping technologies and suitable types of binders or if needed additional additives are to be applied. Both the technology and the type and amount of binder and additives have an impact on the physical and chemical properties of the shapes. Later developments dealt with so-called binderfree molecular sieves and their extended manufacturing process as well as its optimization until they were introduced to the market around 2000. It could be shown, that practically all market relevant molecular sieves can be generated as binderfree material, available in all common shapes, including compact bodies like honeycombs, multi-channel and foam-like structures. Such binderfree material exhibits superior properties over the classical binder containing types as e. g. higher adsorption capacities, more open pore systems combined with faster adsorption kinetics, and less undesired side reactions in certain applications. Due to new challenges from the market, more specialized, tailor-made types of zeolite molecular sieves are required. Such higher specialization can be achieved by applying new types of zeolites or zeolite-like materials, modified synthesis and/or post synthesis treatments, and by modified, to the needs of the application adjusted shaping processes. The optimized zeolite molecular sieves allow more efficient adsorption processes with reduced zeolite molecular sieve amounts combined with smaller and sustainable adsorption plants.

1162 - PHOTO THERMAL DECOMPOSITION OF AMMONIA OVER NI AG SBA 15 CATALYSTS

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Hydrogen is a promising alternative to fossil fuels for the production of energy with zero carbon footprint. The main challenges of hydrogen as the energy vector are its cost effective production from water electrolysis, as well as storage and transportation, which are plagued by low volumetric energy density of compressed or liquefied H2. Ammonia is an attractive source of hydrogen, because it can be produced on a megaton scale, possesses a high hydrogen content (17.8 % w/w), and can be economically stored and transported as a liquid at pressures below 10 bar. Moreover, ammonia decomposition reaction into hydrogen and nitrogen can occur at moderate temperatures and ambient pressure (2NH3 ↔ 3H2 + N2; ΔHR = 92 kJ/mol).[1] Efficient (photo)catalysts for this reaction are still required. The aim of this work is to study the Ni-Ag/SBA-15 catalysts for photo-thermal ammonia decomposition enabled by visible light at low temperatures, thus enabling direct coupling of NH3 decomposition with H2 utilization in the low temperature PEM fuel cells. The SBA-15 ordered mesoporous silica is transparent for visible light, is highly thermally stable[2], Ag has the function of plasmonic antenna for light harvesting and nickel is the active site for ammonia decomposition.[3] Mesoporous ordered amorphous silica SBA-15 was synthesis by hydrothermal method. In a typical synthesis, 8 g of Pluronic P123 triblock copolymer was dissolved in 1.6 M HCl. After complete dissolution of surfactant, 17 ml of tetraethyl orthosilicate was added at 45 °C. The suspension was stirred for 8 h at 45 °C and aged for another 16 h at 80 °C. The obtained gel was hydrothermally treated in a stainless-steel Teflon-lined autoclave at 100 °C for 24h. The final product was washed with distilled water, dried at room temperature and calcined at 550 °C K for 6 h, with the temperature ramp of 1 °C/min.[2]The SBA-15 support was decorated with 2 wt. % of nickel and 10 wt. % of silver using deposition precipitation method.[4] The XRD and N2 physisorption analyses confirmed the amorphous structure and a hexagonal array of pores in SBA-15 according to the low-angle diffraction peaks, together with a narrow pore size distribution between 8 – 10 nm and a specific surface area between 800 – 900 m2 /g. Scherrer analysis revealed silver crystallite size values of ~8 nm. After silver deposition, the specific surface was decreased to approximately 500 m2 /g, but was not further modified when nickel was deposited. This suggests that silver blocks a fraction of the cylindrical pores of the SBA-15, which can steer the Ag into cylindrical shape, thus affecting its plasmonic response. The in-situ UV-Vis analysis of 10Ag/SBA-15 showed a broad LSPR band of metallic silver centered at ~350 nm which extended well into the visible range. The same band was attenuated slightly in the 2Ni-10Ag/SBA-15 catalyst, suggesting close intimacy and possibly alloying between Ag and Ni. Photo-thermal experiments of 2Ni/SBA-15 and 10Ag/SBA-15 showed negligible NH3 decomposition below 300 °C, showing that Ag acts exclusively as a plasmonic antenna and nickel has a low thermo catalytic N-H breaking activity. The bimetallic 2Ni-10Ag/SBA-15 catalyst enabled a stable H2 production rate of 0.42 mmol/gcat*min at 120 °C without external heating and only vis illumination (lamba = 400-700 nm, irradiance of 790 mW/cm2), which could be further accelerated to 2 mmol/gcat*min at 300 °C during photo-thermal operation.

This work paves the road towards realization of highly active ammonia decomposition photo-catalysts, which can be driven by visible light at temperatures, which are directly compatible with H2 PEM fuel cells.

1164 - CLINOPTILOLITE HYDROXYAPATITE COMPOSITE SORBENT PREPARATION AND APPLICATION

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Clinoptilolite, due to its specific porous structure, is good sorbent for many cations, however, the degree of efficiency depends on the type of cations and the availability of a zeolite lattice for exchange. Therefore, the aim of this work is to investigate the possibility of improving the sorption efficiency of clinoptilolite towards nickel (II) and chromium (III) ions from aqueous solutions using composites prepared by synthesis of hydroxyapatite on the clinoptilolite surface. Clinoptilolite/hydroxyapatite composites were obtained by hydrothermal crystallization of calcium-hydroxyapatite in the presence of clinoptilolite at 160°C for 4 hours. The sorbents were prepared in two ways: in the first one, ion exchange was previously performed in order to enrich clinoptilolite with calcium ions (CH1), while in the second, calcium ion was introduced with other reactants into the reaction mixture from which hydroxyapatite crystallized (CH2). Phosphorus, necessary for the crystallization of hydroxyapatite, was introduced as a solution of ammonium hydrogen phosphate. The resulting powders were characterized in detail by X-ray powder diffraction (XRPD), thermal TG-DTG analysis, specific surface area and pore distribution (BET) analysis, as well as by scanning electron microscopy (SEM). XRPD analysis of composites showed that the most abundant mineral in zeolite tuff is clinoptilolite, while the presence of hydroxyapatite was identified in the samples obtained by hydrothermal synthesis. Needle-like crystals of hydroxyapatite on the clinoptilolite surface can be observed at SEM photos and it was concluded that the amount of crystallized hydroxyapatite was greater in sample CH2. The results of thermal analysis showed that zeolite/hydroxyapatite composites CH1 and CH2 are thermally stable at 800 °C and that the total mass loss is a consequence of dehydration due to water leaving the clinoptilolite structure and dehydroxylation of hydroxyapatite. The presence of hydroxyapatite influenced the increase of the specific surface area of the sorbent, to a greater extent in CH2 compared to CH1. The adsorption kinetics of nickel and chromium ions were investigated for both sorbents, and it was shown that the pseudo-second-order Lagergren model describes the adsorption kinetics of metal ions well. The presence of hydroxyapatite on the zeolite surface led to an improvement in the adsorption capacity of both tested ions: from less than 3 mg Ni2+/g for the initial clinoptilolite to 8 mg Ni2+/g for composite CH2; and from 13 mg Cr3+/g of initial sample of clinoptilolite to 24 g Cr3+/g CH2. After 24 h, 95% of chromium ions and 42% of nickel ions were bound from the solution by the CH2 composite, while the initial zeolite bound less than 30% of chromium and 15% of nickel. In addition, desorption of nickel and chromium ions from saturated CH2 composite into pure water and solutions of NaCl and NaEDTA was investigated. The percentage of leached ions into the pure water was less than 6 and 1% for nickel and chromium, respectively. Approximately 23% of nickel and 6% of chromium ions were leached into the NaEDTA solution, while 12% of Ni2+ and less than 1% of Cr3+ were released in NaCl solution. Based on the obtained results, it can be concluded that the presence of hydroxyapatite on the surface of clinoptilote significantly increases the adsorption capacity for chromium and nickel ions.

1174 - SYNTHESIS OF CHA ZEOLITE VIA THERMALLY CONTROLLED MECHANOCHEMISTRY

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Most common ways of zeolite preparation are direct synthesis or interzeolite conversion. Direct synthesis is done by mixing a source of silicon and aluminium with a mineralizer, usually in water. Interzeolite conversion is used to convert one zeolite type material into another, usually a more porous to a less porous one by adding an organic structure directing agent (OSDA) along with a mineralizing agent, though it has been shown the OSDA can in many cases be omitted [1]. Both methods of synthesis usually involve hydrothermal treatment conducted at elevated temperatures [2]. This method is often slow, meaning it takes up to two weeks to obtain a pure product, as was the case with ECR-1 synthesized by J. Song et al. [3]. Furthermore, it has been shown that mechanochemical pretreatment of the reactants preceding the hydrothermal treatment can shorten the reaction time and alter the properties of the products, namely the crystallinity and number of Brønsted and Lewis acid sites [4]. Recently however, the first successful attempt of zeolite synthesis by mechanochemical means using thermally controlled mechanochemistry [5] was reported where MER-, CAN-, GIS-, ANA- and SOD-type materials were obtained via interzeolite conversion of a sodium form of FAU-type zeolite [6].

In an attempt to expand knowledge on this novel approach and to selectively obtain a CHA-type material, herein thermally controlled mechanochemistry was once again utilized for intezeolite conversion of a commercially available FAU-type zeolite. By mixing the hydrogen form of FAU with potassium hydroxide and small amounts of water, pure CHA-type material was obtained after 80 minutes of milling at a frequency of 30 Hz and at 110 °C. Additionally, when the ammonium form of FAU was used, seeds of CHA were introduced to the reaction mixture and pure CHA was obtained after only 55 minutes under the same conditions. When the seeds were omitted, a mixture of MER- and CHA-type materials was obtained. These experiments were conducted at the DESY synchrotron facility where in situ PXRD measurements of the reactions could be performed to identify the exact time when the products formed and for how long they exist in the reaction mixture.

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1177 - INFLUENCE OF ZEOLITE FORM ON ACIDITY AFTER MECHANOCHEMICAL EXCHANGE

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The easiest way to exchange zeolites with various metal cations is from H-form. Since only a few zeolites can be directly synthesized in H-form, an exchange of as-synthesized form (usually with Na+) with ammonium salts is required. Although the calcination process is necessary to remove ammonia and get to the H-form it can also lead to the formation of extra-framework aluminium and a decrease in crystallinity. The loss of crystallinity is then further propagated by the cation exchange. Mechanochemical reactions are the area that is still relatively unexplored in the field of synthesis, functionalization, and characterization of zeolites. Cation exchange with metal salts prone to hydrolysis can prove challenging since high concentrations can lead to the amorphization of zeolite, while lower concentrations can result in low exchange percentages or precipitation of metal oxides. The mechanochemical approach to cation exchange allows us to avoid complex dynamics present in the solution and get zeolites with high metal loadings at the same time. However, due to a lack of research in this area, it is not clear how the choice of parent form affects certain properties of product material. Zeolite for the cation exchange was prepared from the gel of molar composition 4Na2O : Al2O3 : 10SiO2 : 158H2O.[1] In order to minimize the degradation of crystal structure samples were prepared by cation exchange from NH4-form and compared to those prepared from H-form. Cation exchange was performed mechanochemically with acetic hydrate salts of magnesium (II), cobalt (II), nickel (II), and zinc (II). After the exchange, all samples were calcined at 550 °C for 6 hours. Samples were characterized using X-ray powder diffraction, scanning electron microscopy, diffuse reflectance spectroscopy, atomic absorption spectroscopy, vacuum FTIR and D3-acetonitrile desorption so that the effect of parent form on crystallinity, morphology, number, and strength of acid sites, composition, and cation coordination can be observed. Samples exchanged from the NH4+ form had much higher crystallinity than those prepared from H-form even after calcination. They also had better-defined bands in the OH region of FTIR spectra, as well as stronger Brønsted acid sites determined by the amount of D3-acetonitrile, adsorbed at 150 °C (Fig. 1.). Analysis of elemental composition reveals that in the case of samples prepared from H-form most metal cations have the tendency to exchange leftover Na+ in the framework rather than the H+, while in those prepared from the NH4-form NH4+ gets exchanged. That difference in the framework affinity is what ultimately leads to the difference in acidity.

1179 - CO SDA FREE GREEN SYNTHESIS OF SMALL PORE ALUMINOPHOSPHATE

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Hydrophilic microporous materials are known as very promising materials for water sorption-based heat storage and transformation. They need to have a high water uptake at low relative humidity, low temperature of regeneration, low price and good cycling performance [1]. Microporous aluminophosphate adsorbents have some advantages over zeolites used as water adsorbents, like higher water adsorption capacity, and lower desorption temperature due to their hydrophobic-hydrophilic character. The main limitation of these adsorbents is the preparation cost due to the use of the expensive structural directing agents (SDAs). For example, the aluminophosphate with Linde Type A topology that was synthesised hydrothermally with Kryptofix 222 as the SDA et elevated pressure, has the highest water uptake (0.36 g/g) among microporous aluminophosphate adsorbents in the relative pressure range from 0.05 to 0.2 [2].

The use of cheap ionic liquids can increase the availability of aluminophosphate water adsorbents for solar thermochemical energy storage [3], showing that this synthesis approach can be a breakthrough in the low-cost industrial production of these water adsorbents. Aluminophosphate with Linde Type A topology has been in most cases ionothermally synthesised with the use of 1-butyl-3-methy-imidazolium bromide as the SDA and tetramethylammonium hydroxide or amines as co-SDAs [4].

In this study, we present an environmentally friendly co-template-free synthesis route of the small pore aluminophosphate with LTA topology (AlPO4-LTA) by using ionic liquid dimethylimidazolium chloride as the SDA. X-ray powder diffraction showed that pure crystalline AlPO4-LTA was crystallized after one day at elevated pressure. The fact that ionic liquids can be recycled and reused makes this ionothermal synthesis a low-cost green synthesis route.

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1186 - HIGH SILICA FAU AND MOR ZEOLITES SYNTHESIS AND CHARACTERIZATION

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Low Si/Al ratio zeolites are supersaturated with aluminium, have a higher concentration of cations, and have excellent adsorptive properties in terms of capacity, size, and channel network. The addition of structural silicon improves both the hydrophobicity and changes in catalytic acidity [1]. The preferred OSDAs for the synthesis of high silica small pore zeolites with large cavities are cyclic or polycyclic ammonium cations that can fit and stabilize the presence of large cavities [2]. The possibility of obtaining high silica zeolites from the modification of hydrothermal synthesis is attractive due to the possibility of chemical surface adaptation without the deterioration of the channel system by post-synthesis procedures, as observed in obtaining the USY zeolite by ammonia vapour dealumination [3].

Zeolite Y (Na-Y) was synthesized OSDA-free from a gel with molar composition 1 SiO2 : 0.1 Al2O3 : 0.4 Na2O : 16 H2O in a seed-assisted crystallization synthesis. XRD analysis confirms the obtained FAU structure, presenting a cubic shape and average grain size of 0.35 µm (by SEM measurement). The SiO2/Al2O3 ratio was 3.6 (by XRF). It is known that zeolite Y can be synthesized directly with a maximum Si/Al ratio of about 3 [4]. Zeolite Y high silica (Na-Y-HS) was synthesized using OSDA tetrabutylammonium hydroxide (TBAOH) from a gel with molar composition 1 SiO2 : 1/57 Al2O3 : 0.1 NaOH : X TBAOH : 20 H2O, where the experienced 'X' values were equal to 0.4, 0.5 and 0.6 mol. The XRD result showed that only by using 0.6 mol TBAOH it was possible to incorporate more Si atoms into the FAU network, resulting in a crystallinity of 77% compared to the Na-Y sample and SiO2/Al2O3 = 6.0 (XRF). Further details on grain morphology and size are still under investigation.

Mordenite zeolite (MOR) was synthesized from the gel with a molar composition of 30 SiO2 : 1 Al2O3 : 6 Na2O : 780 H2O. The diffractogram shows well-defined characteristic peaks for Mordenite topology. The sample shows grains with ellipsoid shape, average grain size of 2.17 µm (SEM), and SiO2/Al2O3 = 10 (XRF). The preparation of high silica content Mordenite zeolite (MOR-HS) started with the gel molar composition of 30 SiO2 : 0.6 Al2O3 : 6 Na2O : 780 H2O in seed-assisted synthesis (5%). The change in the molar ratio of the gel was made by decreasing the amount of aluminium rather than increasing the powdered silica source, which would decrease the viscosity of the gel and result in a less homogeneous medium, favouring the formation of competing phases, such as ZSM-5. Gels distinct only by the amount of water result in the crystallization of distinct structures [5]. The diffractogram of the sample shows well-defined peaks for MOR, with 79% crystallinity compared with the standard sample, presenting lamellar crystals with around 5.1 µm and SiO2/Al2O3 = 15. All materials are also characterized by N2, CO2 adsorptions and catalytic tests.

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1189 - DIRECT SYNTHESIS OF SN CONTAINING MWW TYPE ZEOLITES AND THEIR PHYSICOCHEMICAL PROPERTIES

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The stannosilicates are gaining more attention due to their unique catalytic features due to their high Lewis acidity in the field of biomass conversions like carbohydrate isomerization reaction and Baeyer-Villiger oxidation. In recent studies, Sn-Beta has shown an excellent catalytic ability in those reactions. However, it has poor hydrothermal stability, a long synthesis time, and requires an undesired chemical like HF, causing an environmental issue.[1] The MWW topological structure can be comparable to overcome those drawbacks. In generally, Sn-MWW zeolites were obtained through post-synthesis by functioning deboronated B-MWW with Sn sources.[2] In this study, we spotlighted the direct synthesis of Sn-containing MWW-type zeolite and their physicochemical properties. The precursors of Sn-MWW were hydrothermally according to the report with a modification.[3] The molar compositions of 1.0 SiO2: 1.4 OSDA: 1/y SnO2: 0.2 BO2: x NaOH: 19 H2O. Here, Si, Sn, and B sources were fumed silica, SnCl4·5H2O, and H3BO3, respectively. Also, hexamethyleneimine (HMI) was used as the OSDA. After vigorous mixing, the gel was autoclaved and crystallized under rotation (40 rpm) at 170 °C for 7 days. Finally, as-made materials were calcined at 550 ℃ for 6 h. Hereinafter, the calcined samples were designated as Sn-MWW-x-y, where x = 0.20 or 0.25 is the Na/Si ratio and y is Si/Sn ratio = ∞, 400, 200, 100, and 50 in the gel. First, the effect of the Sn content in the synthesis gel was investigated. A typical 2D MWW lamellar precursor was obtained when y was more than 100 regardless of x. Thus, obtained 2D lamellar precursors were converted to 3D MWW structure after calcination. At x = 400, the Na content hardly affected the crystallinity. However, it was strongly influenced at a high Sn loading; Sn-MWW-0.25-100 gave much higher diffraction intensities than Sn-MWW-0.20-100. Although their Si/Sn ratios in the product were almost similar (ca. 100), the N2 adsorption indicates that Sn-MWW-0.2-100 showed a lower SBET and Vmicro than Sn-MWW-0.25-100. Furthermore, the SEM observation revealed that Sn-MWW-0.25-100 was a typical uniform sheet-like crystals, while Sn-MWW-0.2-100 contained amorphous particles as well. Hence, it is highly possible that sodium cations participated in the nucleation and crystallization processes and contributed to the transformation of the amorphous gel into the crystalline phase.

In conclusion, the stannosilicate with MWW topology has directly been synthesized with various Si/Sn ratios in an alkali medium. The Sn and NaOH content in the gel plays a key role in the crystallization process of Sn-MWW. Further data on the characterization and catalytic properties will be discussed while comparing with at the poster presentation.

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1199 - MONITORING THERMO MILLING OF NATURAL ZEOLITE CLINOPTILOLITE

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Interzeolite conversion is a zeolite synthesis avenue that uses a crystalline zeolite material as a source of T atoms to obtain another crystalline zeolite [1,2]. It is a principal method for preparation of certain zeolites such as CHA-type materials [3,4]. The benefits of this approach with respect to conventional direct synthesis route from chemicals via amorphous precursors are reduced syntheses periods (enhanced crystallization rate), high yields, and the use of alternative organic structure directing agents (OSDAs) [5]. Besides, interzeolite conversion may provide materials of distinct features compared to the ones from classical synthesis mixtures thus expanding the opportunities of designing zeolite materials with target properties [2,6]. Taking all this into consideration, interzeolite conversion is regarded as synthesis route with high potential in green chemistry era.

Recently was reported mechanochemically induced interzeolite conversion [7] that may improve zeolite production in terms of chemicals used, their quantity, yielded waste and energy consumption as well as costs and thus represents an advancement in environment protection. Mechanochemical methods have gained a lot of attention in the past several years, especially as a possible solution for various drawbacks of solution-based syntheses and processes [8]. The present work brings the previous results to potentially even more environment-friendly level – naturally occurring zeolite mineral clinoptilolite (HEU-type) was used as source material in zeolite synthesis. Clinoptilolite was milled with NaOH, KOH, CsOH and tetramethylammonium hydroxide (TMAOH) with a small amount of added water at 110 °C. The reactions were overseen in situ by synchrotron XRD. In the presence of TMAOH any change takes place and the starting material remains intact for 90 minutes. With NaOH and KOH are observed peaks of the clinoptilolite, but they appear and disappear which may be due to experimental issues. The interzeolite conversion occurred promptly in the milled system using CsOH as mineralizer, yielding ANA after 30 minutes suggesting that the interzeolite conversion is quicker in the presence of CsOH than NaOH, KOH and TMAOH. It is expected that the findings reported here will provide guidelines for designing and conducting further ball milling experiments to achieve even more environment-friendly process of zeolite synthesis.

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1200 - ZEOLITE CATALYZED 1 2 DIBROMINATION OF CINNAMATES USING 1 3 DIBROMO 5 5 DIMETHYLHYDANTOIN AS A BROMINE SOURCE

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Organobromine compounds, also called organobromides, are found in a variety of marine natural products (e.g. aeroplysinin-1, tyrian purple, 14-debromoaraplysillin and 14-debromoprearaplysillin). [1] They are essential synthetic intermediates in the manufacture of derivatives of many natural products, pharmaceuticals, agrochemicals and other fine chemicals. [2] Organobromides are also very useful building blocks for some fundamental chemical transformations such as Grignard reactions, cross-coupling, nucleophilic substitution, etc. [3] Zeolites, as a class of inorganic microporous crystalline aluminosilicate materials, [4] are widely used in numerous large-scale applications as catalysts, ion exchange materials, and adsorbents for organic compounds [5] In addition to these conventional uses, zeolites have also emerged as advanced functional materials applied in the fields of luminescence, electricity, magnetism, medicine and microelectronics, etc. [6] In the present research, various esters of trans-cinnamic acid were chosen for 1,2-dibromination with 1,3-dibromo-5,5-dimethylhydantoin (DBDMH) over zeolites beta, Y and ZSM-5 to study the influence of zeolite pore architecture and the reactant size on the product selectivities and reaction mechanism.

The 1,2-dibromination of a various cinnamates was carried out using a stable, non-toxic, inexpensive bromine source, DBDMH, and a zeolite (beta, Y or ZSM-5) as a catalyst at room temperature. In the present research, methyl trans-cinnamate was chosen to study the molar ratio of DBDMH (1.0 or 1.5 equiv), solvents (aceton, acetonitrile, chloroform, dichloromethane, diethyl ether, diisopropyl ether, dimethyl sulfoxide, ethanol, tetrahydrofuran and toluen), the reaction period (2 h to 24 h) and the quantity of zeolite catalysts (20 and 40 wt%) have been varied. Blank reactions were also carried out in the absence of catalyst. The progress of the reaction was monitored by TLC and by RP-HPLC. Reaction conditions were optimized by use of diethyl ether as solvents with 1.5 molar equivalents of DBDMH and 40 wt% of the catalyst. With the optimal condition in hand, esters were explored as electron-withdrawing groups on the 1,2-dibromination reaction.

The obtained results showed that the cinnamate conversion over 90% was achieved for both zeolite beta and Y in diethyl ether at room temperature. ZSM-5 is not as effective catalyst as the other two. In the absence of a catalyst the reactions were significantly slower. According to the 1H NMR it was found that in all cases the 1,2-dibromination proceeded with anti-stereoselectivity to give the 1,2-dibromide compounds.

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1204 - SN CONTAINING ADORABLE ZEOLITES AS LEWIS ACID CATALYSTS WITH TUNABLE POROSITY FOR THE MEERWEIN–PONNDORF–VERLEY REDUCTION OF CITRONELLAL

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The Assembly-Disasssembly-Organization-Reassembly synthetic strategy opened the way to design‘‘isoreticular’’ zeolites with the same structure of the layers, but variable interlayer connectivities and micropore sizes. Investigation of thus prepared Al- and Ti-substituted model zeolite catalysts in the shape- and chemoselective transformations of organic molecules offers a valuable insight into structure-performance relationships. [1-3] Theoretically, ADOR can be applied to structurally and chemically diverse zeolites, but till now this synthetic strategy was realized only for UTL zeolite in titano- or alumino-germanosilicate form, which limited the scope of reactions catalyzed by “isoreticular” zeolites.

Stanno-silicates are a diverse group of catalysts with impressive activity in a variety of essential chemical reactions (biomass upgrading, Meerwein-Ponndorf-Verley (MPV), Baeyer-Villiger (BV) oxidation, ring-opening of epoxides). The insertion of Sn(IV) into the zeolite structures can be seen as a major advance in the design of solid Lewis acid catalysts that are favourable to the environment [4]. Sn-containing zeolites Beta, MFI, MWW present a remarkable activity and selectivity for a variety of environmentally friendly and sustainable catalytic processes, although there is still a lack in the number of shape selective stannosilicate catalysts compared to the number of available zeolites.

Herein, ADOR approach was elaborated for the preparation of “isoreticular” Sn-containing zeolites based on UOV, IWW and IWR topologies. Structural and textural properties of the catalysts were validated by X-ray diffraction and high-resolution TEM analysis, while the state of Sn sites was addressed using FTIR and NMR spectroscopies of adsorbed probe molecules. Besides expected selective removal of Ge framework atoms, interconversion of “closed”-to- “open” Sn acid sites was observed. This interconversion affected the catalyst activity in MPV reduction of citronellal with isopropyl alcohol.

The parent UOV, IWW, IWR Sn-substituted 12-ring zeolites showed higher conversions of citronellal than 10-ring Sn-MFI with comparable Sn concentration, while mainly isopulegol isomers (selectivity up to 85 %) were formed. Compared to Sn-MFI, the ADORable 8-ring zeolites with high fraction of “open” sites showed not only increased selectivity to targeted product of MPV reduction (up to 76 %), but also 3-fold higher conversion values (60 %). The obtained results suggest Sn “closed” and “open” Lewis acid centers as active sites in citronellal isomerization and MPV reduction, respectively.

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1210 - STRUCTURAL AND PHYSICOCHEMICAL TRENDS IN PHOSPHORUS TREATED CONVENTIONAL AND HIERARCHICAL ZSM 5 CATALYSTS FOR UPGRADING OF FT WAX

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With the world's growing energy demand and increasing environmental issues associated with the use of conventional fossil fuels, the Fischer-Tropsch (FT) process is a commercial process for producing cleaner, alternative fuels. The lack of product selectivity and formation of high-molecular-weight FT-wax from the FT-process adds to the cost and complexity of the overall process, thus reducing the commercial attractiveness of this technology. To increase the economic viability of the FT-process, hydrocracking of FT-wax can be used to convert FT-wax to value-added fuels. This can be achieved using bifunctional catalysts containing a metallic function (Pt) and an acidic support (zeolites).[1, 2]

Zeolite micropores offer excellent shape selectivities in catalytic reactions, however, their small pore size has a severe effect on diffusion limitations and catalyst lifetime. For these reasons, the synthesis of hierarchical zeolites, containing microporous materials with at least two classes of pores (microporous and mesoporous) is helpful to overcome the drawbacks of conventional zeolites.[3, 4] Chemical modification of zeolites, such as phosphorus-treatment, is also known as an efficient method to enhance catalytic activity of the zeolite catalyst, by altering acid sites. The relationship between zeolites and phosphorus is poorly understood and the fundamentals of phosphorus-zeolite chemistry are still under investigation.[5]

In our study, conventional ZSM-5 and hierarchical ZSM-5 nanosheets (ZSM-5-NS) were modified using H3PO4 with a P/Al ratio of 6. The XRD pattern of the P-modified ZSM-5 catalyst indicates the presence of additional reflections, corresponding to AlPO4 species after phosphorus treatment. Solid state 27Al NMR of ZSM-5-NS displayed peaks corresponding to tetrahedral framework aluminium (FAl) and octahedral extra framework aluminium (EFAl). 31P NMR of the phosphorus-treated ZSM-5-NS revelead P-Al interactions in the form of octahedral aluminium interacting with phosphorus, and the disappearance of the peak corresponding to FAl. Phosphorus interacts with FAl, which induces octahedral coordination in aluminium. Furthermore, phosphorus preferentially interacts with EFAl, leading to the formation of AlPO4 species as seen from 31P NMR and XRD results. EELS analysis will be performed to give information on the electronic environment of phosphorus in the zeolite framework.

An in-depth investigation of the structural modification of conventional ZSM-5 and ZSM-5-NS with phosphorus will provide insight into the exact nature of hydrothermal stability, changes in acidity and catalytic performance. The goal of our study is to investigate structural and physicochemical trends in phosphorus-treated zeolites and relate these findings to the catalytic performance for hydrocracking of FT-wax.

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1223 - HIERARCHICAL NANOCRYSTAL AGGREGATE SAPO 34 FOR N BUTANOL CONVERSION TO OLEFINS

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Hierarchical SAPO-34 with nanocrystal aggregate was achieved by applying lower amount of solvent in its hydrothermal synthesis. This synthesis technique is simple and can reduce the waste amount of mother liquor from the synthesis product. Moreover, the expansive mesoporogen is not required. The crystalline material was thermodynamically transformed to the 30-60 μm-size aggregate compacting with 10-20 nm nanocrystal size (instead of well-defined cubic crystal of 12 μm). This hierarchical structure consists of interparticle mesopores between the nanocrystals of SAPO-34.

The hierarchical nanocrystal aggregate SAPO-34 has surface area and pore volume of 418 m2/g and 0.80 cm3/g with high mesopore volume of 0.59 m2/g. The broad mesopore size distribution is between 4-40 nm with the major diameter of 16 nm. The SEM reveals the hierarchical SAPO-34 has aggregate form (30-60 μm) of nanosized crystallites (10-20 nm). This hierarchical structure of SAPO-34 was designed to use as an efficient catalyst in n-butanol conversion to olefins. This reaction is known for easily clogged by coke formation in the catalyst. The goal is to obtain high butene yield with enhance reaction stability.

Bioalcohol is one of reliable renewable energy source in the future bioeconomy. Butanol is the next generation bioalcohol with better properties than lower-carbon alcohols. The butanol can be converted to olefins by dehydration reaction. This sustainable source of olefins is a new route of the chemical building blocks to produce numerous value-added chemicals and polymers, instead of conventional route of fossil feedstock. In this research, the n-butanol conversion reaction was performed at atmospheric pressure, weight hourly space velocity (WHSV) of 3.75 h-1, and reaction temperature of 230-300°C. The hierarchical nanocrystal aggregate SAPO-34 (Hi-SAPO-34) was applied as catalyst. It showed complete conversion with high yield of butene >85%. Whereas the conventional SAPO-34 catalyst exhibited lower conversion of 53% and 72% at the reaction temperature of 230 and 250°C, respectively and lower butene yield of 64%. The higher rate of deactivation was observed with the conventional SAPO-34 because of large diffusion pathway of the crystals (12 μm vs. 15 nm). Evidently, the coke content of the spent Hi-SAPO-34 catalyst is lower by 31% of the spent conventional SAPO-34. At the suitable condition of the reaction temperature 230°C, the Hi-SAPO-34 showed the highest butene yield of 96%, completely conversion, and better catalyst stability. Its shape selective property is essential, and it needs to be balanced with the fast molecular diffusion from the short diffusion path length and the hierarchical structure for the high performance of this catalyst.

Therefore, the hierarchical nanocrystal aggregate SAPO-34 is suggested as a promising catalyst in n-butanol conversion to butene with high purity and lower deactivation rate. The butene can be utilized without further energy-intensive purification. This synthesis technique is recommended as simple, low-cost, and environmentally friendly procedure to obtain the efficient catalyst for this reaction.

1263 - APPLICATION OF HETEROGENEOUS CATALYSIS IN THE CONVERSION OF LIGNOCELLULOSIC BIOMASS

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Lignocellulosic biomass is one of the promising renewable energy sources in obtaining fuel, heat or chemical compounds [1]. It consists of three components, such as: cellulose, hemicellulose and lignin [2]. Research is being conducted on its decomposition in order to facilitate its application to various types of processes [3]. The decomposition of lignocellulose is possible using chemical techniques, such as acidic or alkaline hydrolysis [4]. Mechanical treatment or thermal processes, e.g., gasification, are also possible [5]. One of the most commonly converted forms of biomass into chemicals and fuels is the cellulose fraction. Research is being conducted on its transformation into organic acids using various types of catalysts, including zeolites [6].

In our research, we present the potential use of natural zeolite - clinoptilolite as a matrix to create a catalytic material. Clinoptilolite was modified by ammonium exchange and ion exchange to substitute metals (Fe, Cu and Co) under ultrasonic conditions. Zeolite catalysts were then used in the glucose conversion process, which is the composition of the cellulose fraction of lignocellulosic biomass. The catalytic transformation of glucose with the use of zeolites was performed using the one-pot method at 250°C for 5 hours under increased pressure. Based on the chromatographic analyzes performed with the participation of HPLC-RID, the conversion of the raw material and the selectivity of the products were determined. Based on the obtained results, it was determined that the presence of iron as the active site

leads to the production of lactic acid with a selectivity of 40.3%. It was also noted that cobalt and copper also lead to this organic acid with a selectivity of 35.6% and 36.4%, respectively. On the basis of the performed tests, it can be suggested that the method of obtaining zeolite catalysts based on clinoptilolite may be a cheap and promising catalytic material for the conversion of biomass to organic acids, including lactic acid.

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1267 - INCORPORATION OF TITANIUM IN ITQ 15 AND ITS APPLICATION AS CATALYST

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Zeolite ITQ-15 (UTL) presents a bidirectional channel system of 12 and 14 member rings [1]. The extra-large pore size allows the application of the zeolite ITQ-15 as catalyst in reactions in which large organic molecules are involved without diffusion problems. In addition, the incorporation of titanium in its structure affords redox properties to the zeolite that generates a great interest in different catalytic processes.

Although the presence of germanium in a zeolite could result in an unstable zeolite structure during the calcination process, the incorporation of germanium in the synthesis gel is required to synthetize the zeolite ITQ-15 thus far. This work develops the synthesis of the zeolite ITQ-15 by direct synthesis as titanosilicate, in absence of trivalent compounds, with the lower amount of germanium described in bibliography [2]. Its structural composition presents a molar relation of (Si+Ge)/Ti = 132 and Si/Ge = 7. With this germanium content, the zeolite ITQ-15 is stable during the calcination process. Therefore, for the first time, it is possible to use the zeolite Ti-ITQ-15 as catalyst.

Ti-ITQ-15 (Si+Ge)/Ti = 132) zeolite has been applied as catalyst in the Beckmann rearrangement of cyclohexanone oxime to produce caprolactam [3]. The caprolactam has a high global demand because is the precursor of Nylon 6 filament, fiber, and plastics. As mentioned reaction, catalysed by the Ti-ITQ-15, shows high activity and selectivity values (TON=102, TOF= 105 h-1; S= 100%) towards the obtention of the caprolactam under relatively mild conditions after 6 hours of reaction time.

The transformation of the cyclohexanone oxime into the corresponding amide (caprolactam) takes place efficiently and selectively in the presence of Ti-ITQ-15 zeolite in about 6 hours under smooth reaction conditions (170ºC and 12 bars of N2), showing that ITQ-15 is a very competitive and green catalyst to carry out rearrangement reactions. More specifically the Beckmann rearrangement reaction starting from an oxime to give an amide. On the bases of this result, subsequent studies will be undertaken to further reduce the Ge content and increase the incorporation of Ti in order to exploit the potential of this catalyst in reactions of industrial interest.

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1270 - SYNTHESIS AND CRYSTAL GROWTH MECHANISM OF PST 2 AN ALUMINOSILICATE SBS SBT ZEOLITE INTERGROWTH

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In our recent preliminary work, we have reported the synthesis of an aluminosilicate (Si/Al = 3.1) member of the hypothetical SBS/SBT intergrowth family, denoted PST-2, via the charge density mismatch (CDM) approach using Cs+ as a crystallization ISDA and tetraethylammonium (TEA+) as a CDM OSDA.[1] Spherical aberration corrected (Cs-corrected) scanning transmission electron microscopy (STEM) coupled with an annular dark field (ADF) detector (STEM-ADF) indicates that PST-2 is formed by a ca. 50:50 SBS/SBT intergrowth, but the intergrowth distribution (15-100:0-85) of its two end members is significantly wider compared to the well-studied intergrowth families like MFI/MEL, beta, and FAU/EMT. Interestingly, PST-2 was found to typically appear as long stacks of very thin disk-like crystallites, which is rare among the zeolite crystallite morphologies known to date.

In this study, we present the results from PST-2 synthesis using a total of 14 organoammonium cations as a CDM OSDA to investigate the effect of OSDA size, shape, and charge on the phase selectivity of the crystallization and the intergrowth characteristics of the resulting PST-2 crystallites.[2] The synthesis results show that PST-2 zeolites can be synthesized using six different CDM OSDAs but under the same synthesis conditions (i.e., 7 days of heating under rotation (60 rpm) at 120 °C). We also found that the SBS/SBT intergrowth ratio in PST-2 and its crystallite dimensions can be altered by the crystallization time, as well as by the type of CDM OSDA employed. The distribution of SBS domains in all TEA-PST-2 crystallization time at 120 oC, indicates the similarity of the formation energy of its two end members (i.e., SBS and SBT).

We determined the average stack lengths and average disk numbers, diameters, and thickness of disk-like TEA-PST-2 crystallites in the above series of solid products, using FE-SEM and TEM techniques. These data reveal that the relative growth rate in the a axis of PST-2 crystallites is about three and half times faster than that in the c axis. It thus appears that the crystal growth of PST-2 might take place through the layer-by-layer mechanism, like the case of the FAU/EMT intergrowth family. On the other hand, the ratio (ca. 20) of the stack length of the solid after 1.8 days to that of the fully crystallized TEA-PST-2 was found to be 10 times larger than their disk thickness ratio (ca. 2) . This suggests that the stacking rate of disk-like crystallites is much faster than their crystal growth rate. In addition, since there are no signs of the presence of single or a few disk-like crystallites from any of FE-SEM and TEM images taken here, it is most likely that stacking of PST-2 crystallites appears to occur on a disk-by-disk basis. On the basis of the overall results of our study, we propose a plausible crystal growth mechanism of this large-pore zeolite intergrowth.

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1304 - SELECTIVE HYDROGENATION OF 1 3 BUTADIENE OVER PD NANOCLUSTERS IN 3D GRAPHENE LIKE ZEOLITE TEMPLATED CARBON CATALYSTS

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Selective hydrogenation of 1,3-butadiene is an important chemical process in the production of fuels and polymers. Partial hydrogenation 1,3-butadiene to 1-butene is used prior to polymerization processes for the production of butene polymers. Hydrogenation of 1,3-butadiene preferably to 2-butenes is performed before alkylation processes for the production of high-octane gasoline. We investigated the effects of the clusters morphology and the electronic interaction between the carbon supports on the selectivity to the individual products. The 3D graphene catalysts with different distributions of metal clusters and with different interactions with the surface and the subsequent analysis of the relationships between structure and selectivity/activity were used to obtain an understanding the parameters controlling the selectivity and activity in the hydrogenation process. Structural parameters governing the stepwise insertion of four hydrogen atoms to the two double bonds of 1,3-butadiene were analysed in order to develop catalysts with the tailored selectivity in the hydrogenation reactions.

The well-defined and regular 3D channels system of the faujasite zeolite was replicated into the zeolite templated carbon material with well-defined dimensions and spatial connectivity of the micropores by nanocasting. The faujasite zeolite in the H+ form of the molecular Si/Al ratios 6 was used as a hard template for the preparation of 3D graphene-like microporous carbon material denoted as Y-carbon. Carbonization of the zeolites was performed using chemical vapour deposition with propylene as a carbon precursor [1]. In the process of zeolite nanocasting, carbon atoms were generated along the walls of the regular zeolite micropores. The subsequent selective removal of the structural lattice of the zeolite provided an ordered 3D microporous graphene-like carbon material. The porosity of the carbons was determined by analysis of the adsorption isotherms of nitrogen. High resolution transmission electron microscopy (HR-TEM), and scanning electron microscopy (SEM), were used for imaging the morphology, shape and size of the zeolite, carbon/zeolite and carbon materials and for analysis of metal and metal-oxo clusters. X-ray powder diffraction was used for analysis of the zeolite structure, level of replication of structural ordering of zeolite, spatial arrangement of carbon material and zeolite, and formation of graphene-like structure without sheets layered on top of each other. X-ray Photoelectron Spectroscopy (XPS) was used for analysis of the electronic interaction between the carbon supports and metal clusters.

The effect of the decrease in the Pd cluster sizes to a nanometre and further to a sub-nanometre scale on the activity, selectivity and stability in the catalytic reactions was analysed. The obtained results show that the size of the Pd clusters controls the reaction rate and selectivity in the hydrogenation of 1,3-butadiene to 1-butene and 2-butenes. The study demonstrates how the optimal combination of the strength of the metal cluster interaction with the surface and the optimal size of the clusters provides electronic properties leading to a large improvement in the selectivity/activity in the hydrogenation reaction.

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1308 - PLATINUM NANOPARTICLES ON ZEOLITE TEMPLATED 3D GRAPHENE LIKE CARBON FOR BENZENE HYDROGENATION

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Traditional hydrogenation catalysts for clean hydrogen sources under mild conditions are based on well-dispersed clusters of precious metals (Pt, Pd, Rh), most often on activated carbon or alumina. In this study, we investigate the possibilities of using Pt clusters deposited on a 3D graphene-like organized structure of zeolite-templated carbon for the preparation of hydrogenation catalysts. Zeolite templated carbon (ZTC) materials are characterized by a very high specific surface area, structural stability, accessibility of the entire surface due to the regular organization of the porous structure [1-2]. The structure of ZTC materials is built systematically from hexagonal rings of carbon atoms like a 3D graphene along surfaces on zeolite pore walls with presence of five- or seven-membered rings and various degrees of imperfections forming a 3D inverse replica of the zeolite channel structure [1-2].

Our findings suggest that 3D graphene-like microporous Y-carbon and β-carbon materials synthesized in a zeolite template with a specific surface area comparable to the theoretical surface area of graphene and curved surface accessible through the channel system enable accommodation of very high concentration of well dispersed Pt nanoparticles. With a comparable Pt loading in the catalysts (∼3 wt.%) and a similar size distribution of Pt clusters, Pt/Y-carbon provides only slightly increased activity compared to Pt on standard supports Al2O3, SiO2 and activated carbons. However, the Pt/Y-carbon catalysts can be prepared with a very wide range of metal loadings up to at least 25 wt.% with a very good metal particles dispersion comparable to the loading for materials with 3 wt.% Pt. Due to the 3D organised open porous structure, allowing access to the active centers, the TOFPt values are the same even for very high Pt loading. The catalytic activity of Pt/Y-carbon is thus directly proportional to the Pt loading, and the high concentration of active Pt sites provide extraordinary high activities in the hydrogenation of benzene to cyclohexane. The Pt nanoparticles supported on zeolite templated Y-carbon is an example of a new class of ZTC metal supported catalysts providing a very high concentration of metal sites on well accessible 3D organized porous support.

This study thus illustrates a concept for the formation of catalysts with a very high concentration of supported metal clusters for others heterogeneously catalysed reactions. It can be assumed that, as was shown for Pt/Y-carbon, the structure of ZTC materials can be exploited for the deposition of other active metal nanoparticles.

Acknowledgments

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1317 - PRELIMINARY INVESTIGATION OF THE HG(II) CHLORIDE COMPLEXES SORPTION ONTO THE FABRICATED MODIFIED NATURAL ZEOLITE CLINOPTILOLITE

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Natural and especially anthropogenic sources of mercury are of the great concern because of its well-known toxic effect on the entire ecosystem. Special attention is paid to the former places of mercury ore exploitation and roasting, and one such example is the area of the Idrija mine in Slovenia, the second largest mining district in Europe after Almadén in Spain. Although the mine ceased operations almost three decades ago (in 1995), the consequences are still noticeable. For instance, mercury pollution was found in the Gulf of Trieste in Italy as a result of its constant leaching from the mentioned area and its transport by the Idrijica and Soča-Isonzo rivers. In seawater, soluble Hg(II) chloride complexes are formed, as well as mercury methylation in the sediment. In this way, mercury becomes easily available to enter the food chain via phytoplankton, which represents the starting point for its bioaccumulation and biomagnification. Therefore, it is extremely important to prevent the spread of pollution in the most economically and ecologically efficient way. For this purpose, the use of natural materials such as zeolites is preferred due to their easy availability, wide distribution and environmental acceptability. Thus, the purpose of this paper is to examine the effectiveness of fabricated modified natural zeolite clinoptilolite originating from the Vranjska Banja deposit in Serbia for the removal of mercury from the mercury(II) chloride solutions which simulate mercury-contaminated seawater. The modification was carried out in two stages, in an acidic medium with a solution of Fe(NO3)3×9H2O, and then in an alkaline medium with a solution of Na2S×9H2O. Physico-chemical characterization revealed an increase in the amount of iron by 2.5 times and sulphur by 12 times. The SEM-EDS analysis confirmed the deposition of iron sulphide species on the zeolite surface. The XRPD analysis revealed a slight loss of crystallinity as a result of desilication, i.e. treatment in an alkaline medium, which also leads to an increase in negative charge. Namely, in the first stage of modification in an acidic medium, fixation of iron is achieved on the surface of natural zeolite. In the second phase, fixed iron acts as a support for the stabilization of sulphur species. Therefore, the fabricated material should have increased sorption properties towards mercury species since sulphide species are known to be the most common scavengers of mercury in nature.

The sorption efficiency of Hg(II) chloride complexes was tested under different experimental conditions. The optimum pH was found to be 2 and the solids/liquid ratio was 6 g/L. Kinetic experiments established that most Hg(II) was sorbed within 120 minutes. Under the aforementioned optimal conditions, a maximum sorption capacity of 0.54 mmol/g of the modified zeolite was achieved, which is 7.4 times more compared to the natural zeolite. In addition, at co(Hg)<1 mmol /L, the removal efficiency of modified zeolite for Hg(II) complexes was even 99%, while of natural zeolite it was only 10%. The obtained results clearly indicate that the newly formed active sites containing iron sulphide species as well as the increase in the net negative charge are responsible for the significantly improved sorption properties. Ultimately, the obtained results completely justify the implementation of the modification procedure.

1339 - NANOHYBRID BASED ON BIOLOGICAL RENEWABLE LIGNIN AND ZIRCONIA

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Lignin from biomass is one of the most perspective molecules for the preparation of hybrid sustainable biomass-inorganic materials. However, the valorization of lignin is currently limited to 95% worldwide. The complex polymer structure of lignin is rich in aromatic structures such as three principal building blocks, p-hydroxyphenyl (H), guaiacol (G), and syringyl (S), and could be a promising carbon precursor source [1]. Aromatic structure enables lignin to act as a template in the synthesis of mesoporous inorganic materials. For example, lignin was used as a template for the synthesis of mesoporous TiO2. [2] One of the interesting inorganic materials is zirconia. It is a chemically stable, non-toxic, and low-cost rare-earth oxide that is in widespread use as a high-performance engineering material. Exists in three crystal forms: monoclinic, tetragonal, and cubic. Possess a wide bandgap energy between 3.25 eV and 5.1 eV and due to the wide bandgap photoexcited electrons can rapidly recombine with holes and retard the overall solar energy conversion efficiency [3]. One of the solutions for narrowing the bandgap is doping the material with carbon-rich material, for example, lignin. With this doping, we will have a material with improved photocatalytic efficiency. Zirconia-lignin nanohybrid due to its complex lignin structure will have mesoporous characteristics. In this study, we have developed a facile method to synthesize zirconia-lignin nanohybrid (Figure 1.) with the potential multifunctional application. New material was evaluated by means of morphology, phase composition, porosity, and catalytic activity. The formation mechanism of mesoporous zirconia-lignin nanohybrid was also proposed.

1349 - SELECTIVE CATALYTIC OXIDATION OF AMMONIA OVER COBALT SILICATE MWW TYPE ZEOLITES

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Selective catalytic oxidation of ammonia (NH3-SCO), i.e., $2NH_3 + O_2 \rightarrow N_2 + 2H_2O$, is a promising technology that can remove air pollutant ammonia due to its economic and environmental advantages [1]. Among various metal catalysts for NH3-SCO, zeolite-supported metal catalysts are widely studied due to a lot of advantages of zeolite as a support, such as hydrothermal stability, acidity, and selectivity [2]. In this study, we prepared three-dimensional (3D) MWW and 2D cobalt silicate delaminated MWW layers (Co-DML) by the single-step hydrothermal treatment of the borosilicate MWW zeolitic precursor with a 1.0 M cobalt nitrate solution at 80–160 °C for 4 days. Then, the synthesized catalysts were characterized by various analytical techniques, such as powder XRD, N2 sorption, FT-IR, UV-DRS, ICP-OES, Co 2p XPS, STEM-EDS, NH3-TPD, and H2-TPR. Finally, the synthesized catalysts were applied to the NH3-SCO to evaluate their catalytic activity. Powder XRD patterns of Co-DML-x, where x represents the hydrothermal treatment temperatures, i.e., 80, 100, 120, 140, and 160 °C, showed that the increase of the hydrothermal temperatures promoted the structural transformation of 3D MWW into delaminated 2D MWW layers. Co-DML-x had no X-ray peaks for metallic Co or cobalt oxide, which indicates that Co particles were highly dispersed in all the Co-DML-x. In N2 sorption isotherms, the micropore area decreased and the external surface area increased as the hydrothermal treatment temperature increased owing to the dimensional transformation of 3D to 2D MWW, which was consistent with the powder XRD patterns. IR spectra in the structural region of Co-DML-x showed the increasing IR peaks for Si–O–Co at 1025 cm–1, indicating that the substitution of the framework Co instead of B species was improved by increasing the hydrothermal temperature. However, IR peak assigning to Co oxide at 664 cm–1 was displayed in the IR spectra of Co-DML-160 likely due to the excess amount of Co species that could not be inserted into the framework. Nevertheless, all the STEM-EDS images of Co-DML-x exhibited the highly dispersed Co species regardless of framework Co and Co oxide. H2-TPR analysis over Co-DML-x showed the following order of reducibility of Co-DML-x: Co-DML-100 < Co-DML-120 < Co-DML-140 < Co-DML-160, which is likely due to the increasing framework Co species in Co-DML-x. When applying Co-DML-x in NH3-SCO, NH3 conversions over Co-DML-x catalysts as a function of reaction temperatures, 200, 300, 400, and 500 °C, were improved as the hydrothermal temperatures increased, especially, Co-DML-160 showed the highest NH3 conversion, which can be rationalized by the increase of framework Co species and enhancement of reducibility. Therefore, it can be suggested that Co-DML-160 can be promising catalyst for NH3-SCO reaction in the future.

1350 - SYNTHESIS OF STANNOSILICATES BY INTERZEOLITE TRANSFORMATION AND THEIR CATALYTIC ACTIVITY IN GLUCOSE CONVERSION

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Cascade catalytic conversion of biomass-derived carbohydrates to 5-hydroxymethylfurfural (HMF) is an important reaction to produce raw materials for useful chemicals without using fossil fuels [1]. Stannosilicates have been regarded as promising catalysts for biomass conversion due to their Lewis acidic properties caused by framework Sn species [2]. In this study, we prepared three-dimensional (3D) MWW (Sn-MWW(3D)), 2D MWW (Sn-MWW(2D)), and their interzeolite transformed BEA-type (Sn-BEA(IT)) stannosilicates, and compared their catalytic acitivity in glucose conversion. Sn-MWW(3D) was synthesized by following the method reported elsewhere. Sn-MWW(2D) was prepared through the conventioanl delamination procedures of Sn-MWW(3D). Sn-BEA(IT) was synthesized by heating a dried mother gel consisting of Sn-MWW(3D), siliceous beta seed, TEAOH, and NH4F at 190 °C for 12 h. For comparison, Sn-BEA(Top) was also prepared by consecutive acid dealumination and isomorphic substitution of Sn into the dealuminated BEA zeolite. These stannosilicates were characterized by powder XRD, TGA/DTA, N2 sorption, ICP-OES, FT-IR, and STEM-EDS. Then, the prepared catalysts were applied to the glucose conversion at 160 °C for 1–24 h. Both Sn-MWW(3D) and Sn-BEA(IT) clearly exhibited their powder XRD patterns for MWW and BEA structures, respectively. However, Sn-MWW(2D) did not show any characteristic XRD patterns due to its delaminated property. The fully crystallized Sn-MWW(3D) and Sn-BEA(IT) resulted in the reasonable organic contents with ca. 11 and 15 wt.%, respectively. Their N2 sorption data showed the type-I isotherms, but Sn-MWW(2D) showed the type-IV pattern owing to the interparticle void volume of 2D layers. The Sn contents of these stanosilicates determined by ICP-OES were analyzed as follows: 4.2, 2.9, and 4.8 wt.% for Sn-MWW(3D), Sn-MWW(2D), and Sn-BEA(IT), respectively. IR spectra in structrual region exhibited that the intensity of the characteristic peak for Si-O-Sn was as following order: Sn-MWW(3D) > Sn-BEA(IT) > Sn-MWW(2D). In addition, Sn-MWW(2D) showed the most agglomerated Sn species in STEM-EDS images. In the IR spectra in the hydroxyl region, Sn-MWW(2D) also showed the most intense IR peak for silanol groups due to its delminated feature. Pyridine adsorption IR spectra showed the following order of Brønsted and Lewis acidities: Sn-MWW(3D) > Sn-BEA(IT) > Sn-MWW(2D), and Sn-MWW(2D) > Sn-BEA(IT) > Sn-MWW(3D), respectively. Sn-MWW(3D) showed the highest glucose conversion and 5-HMF yield during all reaction times among the Sn catalysts prepared in this study because of the highest Brønsted and the second-highest Lewis acidity. Sn-BEA(IT) exhibited the second-high initial frutose yield, but the highest fructose yield at 24 h of reaction time owing to the higher Lewis aicdity than Sn-MWW(3D). Sn-BEA(IT) also showed the higher catalytic perforamnce than Sn-BEA(Top) due to its higher acidity. Interstingly, Sn-MWW(2D) exhibited the poorest glucose conversion performance, which is probably due to its high concentration of silanol groups inducing extreme hydrophilic character.

1357 - CORE SHELL SSZ 13@AL2O3 ARCHITECTURE A STRATEGY TO BOOST PD CATALYZED PASSIVE NOX ADSORPTION PERFORMANCE

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Nitrogen oxides (NOx) from the exhaust of vehicles are considered one kind of hazardous air pollutant that can cause photochemical smog and harm to human health. The selective catalytic reduction of NOx with NH3 (NH3-SCR) is recognized as the most efficient technology to eliminate NOx at a temperature above 200 °C. However, most NOx is emitted during vehicle operation at a temperature below 200 °C (i.e., cold-start period). To circumvent the NOx emission during the cold-start period, a passive NOx adsorber (PNA) is proposed and collocated with the NH3-SCR catalyst. In the procedure, the PNA can trap NOx at temperatures below 200 °C and desorb the NOx when the SCR catalyst is aroused to work efficiently [1].

Numerous efforts have been dedicated to improving the performance of PNA materials. According to different supports, PNA materials can be divided into two parts: one is metal-supported oxides, and the other is metal-modified zeolites. The potential of γ-Al2O3, ZrO2/CeO2 supported Pt or Pd materials was exploited for low-temperature PNA applications, the high desorption temperature, and the stability of metal oxide supports [2]. In comparison, Pd-based zeolites (Pd/zeolites) exhibited superior NOx adsorption efficiency and capacity for low-temperature NO adsorption, due to their unique porous structure and good thermal/hydrothermal stability of zeolites. Moreover, Pd/zeolites demonstrated excellent hydrothermal stability and poisoning resistance [3]. It is noteworthy that the framework structure of the zeolite (i.e. CHA, MFI, or BEA) affects the PNA performance of the Pd/zeolite materials [4]. The isolated Pd2+ sites (Pd2+ and [Pd(OH)]+) can be stabilized in the small pore of zeolites, which prevents the formation of bulky PdO during hydrothermal aging. Thus, Pd/SSZ-13 exhibited the highest hydrothermal stability among the Pd/SSZ-13, Pd/ZSM-5, and Pd/Beta with similar Si/Al ratios. The SSZ-13 support with a low Si/Al ratio possesses a higher concentration of ion exchange sites, which promotes the formation of more active Pd species and contributes to excellent PNA performance. However, severe hydrothermal aging may cause dealumination and subsequent agglomeration of large PdO particles in Al-rich SSZ-13, resulting in the inevitable deactivation of Pd/SSZ-13. Therefore, it is highly desirable to develop a method to prepare Pd/SSZ-13 zeolites that can generate abundant active Pd2+ species for NOx adsorption and show superior hydrothermal stability and poisoning resistance.

In this work, a Pd-based core-shell material consisting of SSZ-13 core and γ-Al2O3 shell (Pd/(SSZ-13@Al2O3)) was constructed as support for NOx adsorption [5]. The physicochemical properties of prepared Pd-based SSZ-13 zeolites were systematically characterized using techniques such as N2 physisorption, STEM-EDX, 27Al MAS NMR, NH3-TPD, XPS, and H2-TPR. The preparation of Pd/(SSZ-13@Al2O3) under high-temperature calcination conditions is beneficial to the dispersion of Pd species and the generation of more active Pd species. The core-shell structured material facilitated the dispersal and stabilization of the active Pd2+ species. Compared to Pd/SSZ-13, Pd/(SSZ-13@Al2O3) showed significantly improved NOx storage capacity, moderate desorption temperature, excellent hydrothermal aging stability, and resistance to phosphorus poisoning. This study provides a design concept for preparing Pd-based zeolites with high tolerance and high stability for cold-start application.

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1373 - DISCLOSING THE PECULIAR PHASE CHANGE BEHAVIOR OF PERFLUORINATED MIL53(AL) METAL ORGANIC FRAMEWORK THE EFFECT OF TEMPERATURE AND CO2 ADSORPTION

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Carbon Capture and Storage (CCS) strategies play a central role in mitigating carbon dioxide (CO2) emissions. Solid adsorbents for post-combustion carbon capture appear to be a promising solution due to their easier application into existing facilities [1]. Among the materials potentially able to overcome the state-of-the-art technology based on aqueous amines, Metal-Organic Frameworks (MOFs) attract an increasing attention due to the ease in tuning their structure toward a more selective CO2 binding and a lower energy consumption process. A peculiar subclass of MOFs is represented by compounds featuring phase-change accomplished adsorption events, usually evidenced by sudden increase in the adsorbed amount in a narrow pressure region, generating what is experimentally referred to as a S-shaped adsorption isotherm.[2] These materials can afford superior separation performance with a reduced energy penalty.

We recently proposed a facile synthetic method to prepare a perfluorinated form of the well-known MIL53(Al) MOF (hereafter F4-MIL53).[3] The material was thoroughly characterized by several physico-chemical methods. In particular, experimental characterization techniques, such as powder XRD and thermogravimetric analysis, have been coupled with more advanced experimental tools, including spectroscopies (IR and SSNMR), volumetry and microcalorimetry, to finely study the F4-MIL53 features, in particular focusing on the role of fluorine atoms and, most of all, on the flexible behavior of this framework, a major peculiarity of the MIL53 family. Unexpectedly, the breathing capability of F4-MIL53, induced by both specific host-guest interactions and temperature, was detected by using different experimental techniques. Even if a similar behavior is already known for non-fluorinated MIL53, some interesting differences came out: i) thermally induced phase transition can be obtained at much higher temperatures in F4-MIL53 (ca. 500 K, with minimal hysteresis for the reverse transition compared to the non-fluorinated MOF); ii) adsorption induced phase transitions can be triggered by different adsorbates, including application-relevant molecules as CO2. The CO2 adsorption was studied with both volumetric and gravimetric adsorption-desorption measurements. The peculiar host-guest interaction, resulting in an enlargement of the pores, was responsible for a defined step in the isotherm in the 0-5 bar pressure range (T range = 195-313 K). Moreover, fast adsorption/desorption kinetics and complete reversibility makes F4-MIL53 an excellent candidate for applications in pressure-swing based capture-release processes.

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1374 - MONOLITHIC METAL ORGANIC FRAMEWORK CALF 20 COMPOSITE FOR ENHANCED CO2 ADSORPTION

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The increase of CO2 concentration in the atmosphere, which is one of the greenhouse gases, has a great impact on the environment and climate change. One of the approaches to reduce the CO2 concentration is its selective capture and utilization. Particular class of the materials which are thoroughly studied for adsorption of gases are metal-organic frameworks (MOFs) − porous, crystalline solids composed of metal nodes and ligands. These materials have large surface area and porosity, while also can be designed for a wide range of applications. Usually, MOFs are synthesized in microcrystalline (powder) form limiting theirs practical usability. Therefore, to enhance the applicability, MOFs are mechanically structured or shaped into the "macroscopic architectures" or prepared as composites, monolithic macrostructures, membranes, etc. [1,2].

CALF-20 is a small-pore MOF composed of layers of zinc triazolate pillared with oxalate linkers [3]. This material is stable, preferentially captures CO2 over H2O and is easily synthesized from relatively cheap starting materials. Recently, CALF-20 has been used as an CO2 adsorbent in cement plant [4].

Herein, we report on the investigation of the synthesis of the CALF-20 by recrystallization from ZnO or Zn(OH)2 monolithic/composite structures. Zn(OH)2 monolith was prepared by a sol-gel method with polyacrylic acid and propylene oxide [5]. Structured ZnO was made from resorcinol-formaldehyde (RF) monolith template [6,7]. The third type of the monolithic structure is produced by one-pot sol-gel method where RF and SiO2 after carbonization create carbon-silica matrix containing ZnO crystals [8].

The syntheses of CALF-20 materials were then done by reacting solution/suspension of oxalic acid dihydrate and 1,2,4-triazole with structured ZnO at room or higher temperatures. Obtained materials were characterized with XRD powder diffraction, adsorption isotherms for N2 and CO2, scanning electron microscopy and thermogravimetric analysis to prove that CALF-20 retained its crystallinity and distribution in the monolith as well as the accessiility of the pores for CO2 gas.

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1365 - EFFICIENT MICROWAVE SYNTHESIS OF NANO-ZEOLITE β WITH ENHANCED ACID SITES FOR LIQUID-PHASE ALKYLATION OF BENZENE WITH ETHYLENE

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Ethylbenzene is an essential primary organic chemical raw material, mainly used in the production of styrene. The liquid phase alkylation of benzene and ethylene to produce ethylbenzene is currently the mainstream and most widely used ethylbenzene preparation technology due to the relatively low reaction temperature (generally not more than 270 °C), excellent ethylbenzene selectivity and ethylbenzene quality. Zeolite β has become the widely used active component of zeolite-based catalysts in the liquid-phase alkylation of benzene with ethylene due to its inherent unique three-dimensional 12-membered ring pore structure and appropriate acid properties. The primary synthesis method of zeolite β is the traditional hydrothermal synthesis using tetraethylammonium hydroxide (TEAOH) or tetraethylammonium bromide (TEABr) as the structure-directing agent. High template dosage, long synthesis time, the high water content in the system, low molecular sieve yield and other factors lead to its high production cost and energy consumption. Due to the significant industrial application of zeolite β, many researchers have paid attention to improving its existing synthesis technology, increasing synthesis efficiency, shortening crystallization time and reducing synthesis cost and energy consumption. Therefore, due to the remarkable industrial application of β zeolite, improving its existing synthesis technology, improving synthesis efficiency, shortening crystallization time, and reducing synthesis cost and energy consumption have attracted the attention of many researchers.

This work proposed a strategy for efficient microwave synthesis of nano-zeolites β suitable for large-scale industrial production[1]. Considering the characteristics of microwave synthesis, the synthesis of β zeolites was carried out in a laboratory microwave reactor to study the effect of synthesis parameters, such as n(NaOH)/n(SiO2), n(TEAOH)/n(SiO2), n(H2O)/n(SiO2) and crystallization time and temperature on the microwave system. The experimental results showed that nano-zeolite β with high crystallinity could be synthesized under the crystallization conditions of 100 °C for 8 h and 135 °C for 16 h. Compared with conventional hydrothermal synthesis, the water content required for microwave synthesis of zeolite β can be reduced by 20%, contributing to a significant increase of 8% in one-way yield. Furthermore, the crystallization temperature can be reduced by 17%, and the crystallization time can be significantly shortened by more than 50%, indicating that energy consumption will be reduced meaningfully. The characterization results suggest that β zeolite synthesized by microwave has a better specific surface area (626 m2/g) and micropore volume (0.255 cm3/g), as well as higher Brønsted acid sites and Brønsted/Lewis (B/L) value. In benzene and ethylene's liquid phase alkylation reaction, microwave β zeolite shows excellent catalytic activity. It shows higher selectivity of ethyl products and a lower selectivity of heavy products at different reaction temperatures. The texture properties and acidity of β zeolites synthesized by microwave method are significantly improved so that its low-temperature performance in liquid phase alkylation reaction can be enhanced, which is the increase of acid sites so that the catalyst has more active sites to convert more ethylene ultimately, at the same time, the enhancement of pore properties so that the diffusion upgrade makes raw materials and products can be easier to enter and leave.

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1372 - SYNTHESIS OF POLYCYANOMETALLATE COMPLEXES IN ZEOLITE CAVITIES

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Zeolites are a class of porous materials which are comprised of tetrahedra linked via oxygen vertices building a framework. In all silica materials the framework is electrically neutral while the presence of a trivalent T atom such as Al3+ generates negative a framework charge which is compensated by the presence of cations [1]. The cations located in zeolite cavities can be exchanged with other cations. This is usually done by suspending the zeolite in a solution of the desired cation and stirred for a number of cycles to ensure ion-exchange completeness. Those cations can also react with ligands to synthesize complex compounds, such as polycyanometallates. For example, Taylor et al have synthetized hexacyanocobaltate(III) anion ([Co(CN)6]3-) inside the cavities of zeolite Y by treating the Co-modified zeolite with a methanolic solution of sodium cyanide at room temperature for 2-4 days, and have used it successfully for reversible oxygen binding [2].

The aim of this research was to prepare new polycyanometallate anions of transition metals inside of zeolites with different pores sizes. Nickel(II) chloride (NiCl2), cobalt(II) nitrate (Co(NO3)2), manganese(II) chloride (MnCl2), copper(II) nitrate (Cu(NO3)2) and iron(II) sulphate (FeSO4) were used alongside potassium cyanide (KCN) and sodium forms of zeolites Y (FAU) and LTA. Products were identified via infrared spectroscopy (IR) and powder X-ray diffraction (PXRD). Due to the presence of C≡N vibrations in the polycyanometallate compounds, characteristic vibrations were observed in the 2000-2200 cm-1 range and were compared to values present in the literature. PXRD analysis was used to ascertain the crystallinity of the product and whether the zeolite structure remained intact.

Polycyanometallate complexes were identified in samples containing zeolite Y and manganese(II), iron(II), cobalt(II) and nickel(II). By using the characteristic C≡N vibrations of the complexes in the IR range, the identified products are hexacyanomanganate(III) anion, [Mn(CN)6]3-; hexacyanoferrate(II) anion, [Fe(CN)6]4-; hexacyanocobaltate(III) anion, [Co(CN)6]3-; tetracyanonickelate(II) anion, [Ni(CN)4]2-; and nickel(II) cyanide, Ni(CN)2. No polycyanometallate complex of copper(II) was obtained. The crystal structure of zeolite Y was preserved. On the other hand, samples containing zeolite A with the same metals exhibited no C≡N vibrations, meaning that no polycyanometallate complexes are present in those systems. As with zeolite Y, the crystalline structure of zeolite A was preserved in all cases except for the sample containing copper(II) which was amorphized.

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CATEGORY: AIR AND WATER CLEANING

1017 - ON THE ADSORPTION OF CIPROFLOXACIN BY CLINOPTILOLITE AND USE OF NON THERMAL ATMOSPHERIC PRESSURE PLASMA FOR REGENERATION OF THE SPENT ZEOLITE

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The use of antibiotics constantly increases which has a notable negative impact on water bodies. Ciprofloxacin (CIP) is widely applied antibiotic in both human and veterinary medicine, as well as in a livestock breeding. Due to its extensive use, CIP has been found in wastewater effluents in a wide concentration range from ng to mg dm^(–3). An extremely high concentration of up to 50 mg dm^(–3) has been found near drug manufacturing plants [1]. Since CIP, as well as many other pharmaceuticals, cannot be efficiently removed from wastewater streams by conventional wastewater treatments, it is of a great importance to find an acceptable method for their removal.

This study reports the use of natural calcium-rich clinoptilolite (CLI) for the adsorption of CIP and regeneration of the spent adsorbent (CLI-CIP) by non-thermal atmospheric pressure plasma (NTP). The results show that the CLI possesses a high adsorption efficiency in removal of CIP at 283, 288 and 293 K in a slightly acidic medium (pH= 5) for the initial concentrations from 15 to 75 mg dm^(–3). The CIP adsorption by CLI follows the Lagergren's pseudo-second-order kinetics and it can be described well by the Langmuir isotherm model. For all studied temperatures and initial concentrations more than 85% of the CIP is removed within the first 10 minutes. The results also indicate that the CIP adsorption mechanism includes two phenomena: 1) electrostatic interactions between negatively charged aluminosilicate lattice and cationic form of CIP species and 2) ion-exchange reaction.

The use of NTP for the regeneration of CLI-CIP was based on the assumption that NTP generates highly reactive species which can induce a cleavage of the bonds formed between active sites on the CLI surface and CIP, and also induce the CIP decomposition. The NTP treatment was performed for a short time, with a low energy consumption, and without using the additional chemicals. All these make the procedure acceptable not only from economical point of view but also regarding environmental issues [2].

A surface dielectric barrier discharge plasma source was used for the treatment of CLI-CIP. The regeneration study was consisted of five successive adsorption/NTP cycles. Powder X-ray diffraction and Brunauer–Emmett–Teller surface area analyses confirmed that the plasma treatment did not influence the CLI lattice nor its textural properties. Moreover, X-ray photoelectron spectroscopy confirmed that the NTP reduces carbon content in the regenerated CLI for more than 90% and that the plasma reactive species are involved in the CLI regeneration process.

The obtained results strongly support the applicability of the NTP treatment in regeneration of zeolite-based adsorbents used in pharmaceutical removal from wastewater.

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1029 - ELECTROCOAGULATION COUPLED WITH SYNTHETIC AND NATURAL ZEOLITE IN WASTEWATER TREATMENT – ELECTRODE SURFACE AND EFFICIENCY ANALYSIS

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Natural and synthetic zeolites are well known as a promising polishing step in wastewater treatment, based on their adsorption and ion-exchange properties. However, the composition of wastewater is becoming more and more complex, thus application of natural and/or synthetic zeolite in wastewater treatment as the stand-alone process is not enough to obtain satisfactory effluent quality. Nowadays, the increasing interest of many scientists is focused on developing hybrid or combined processes, which combine zeolite with other physical, chemical or biological processes, carried out simultaneously or sequentially, in order to obtain enhanced treatment efficiency and to overcome the limitations of single processes. An example of such a process is electrocoagulation combined with zeolite, natural or synthetic. Namely, electrocoagulation is also recognized as one the most cost-effective treatment process able to efficiently treat wastewater from different sources. By inserting the two electrodes in an electrochemical cell and by introducing direct current, the coagulant is formed “in situ”, thus treatment mechanism includes electrochemical reactions, coagulation/flocculation and flotation. Combining electrocoagulation with zeolite, natural or synthetic, may enhance the treatment efficiency of wastewater, especially in the case of using a real wastewater source.

In this paper, synthetic and natural zeolite are coupled with electrocoagulation (performed simultaneously) in order to obtain efficient wastewater treatment taken from a local municipal wastewater treatment plant. Special accent is done on analysing the change on electrode surface in order to detect the type of corrosion behaviour of aluminium alloys electrodes (anode and cathode) in the presence of natural or synthetic zeolite at different operating conditions (different pH, addition of electrolyte NaCl and Na2SO4 and different contact time). The microscopic analyses are performed by using a light microscope MXFMS-BD, Ningbo Sunny Instruments Co. Images were taken with a Canon EOS 1300D digital camera connected to the microscope at a magnification of 50 times. Also, electrode consumption was determined by weighing the electrodes on an analytical balance and compared with removal efficiency expressed through the determination of chemical oxygen demand.

Results of microscopic electrode surface analysis confirm pitting corrosion, which is more evident at the increased contact time, as more electrode dissolution occurs, thus the highest anode consumption is obtained. However, cathode consumption is also detected and is more pronounced with the addition of synthetic zeolite, at an alkaline condition and at a longer contact time. Probably the zeolite particles, besides their role as an adsorbent and ion-exchanger, may act as abrasive on the electrodes surface and enhance electrode dissolution by damaging the electrode surface layers of oxides/oxyhydroxide/ hydroxides. On the other side, the highest removal efficiency measured through chemical oxygen demand is obtained at acidic conditions, with the addition of synthetic zeolite and at shortened contact time. Thus, the optimal condition needs to be defined through optimization, which takes into account all influencing factors (pH, type of zeolite and electrolyte, chosen contact time) on removal efficiency, electrode consumption, and the residual amount of aluminium in the effluent in order to prevent secondary pollution. To obtain sustainability of this coupled process, further research should be focused on the investigation of the waste material as electrodes. Also, the production of hydrogen during electrocoagulation should be incorporated in a way to reduce the used energy, in order to achieve competitiveness in the final application.

1034 - IMMOBILIZATION OF CARBENDAZIM AND SIMAZINE USING ZEOLITES AND ZEOLITE CARBON COMPOSITE

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The rapid development of the economy, urbanisation, and the need to increase world food production is leading to continuous river and groundwater pollution and seriously damaged ecosystems due to the overuse and misuse of pesticides. There are few technologies for the removal of pesticides, and utilization of adsorbents is one of the most widely applied. Among the adsorbents used for water purification, zeolite-based adsorbents deserve special mention due to their efficiency, capacity, and applicability on a large scale. This study aimed to investigate the adsorption of simazine and carbendazim using zeolites and zeolite-carbon composites.

In the study, zeolite type X (X-FA) and zeolite-carbon composite with zeolite type X (X-C), obtained by conversion of fly ashes, were used. Zeolite was synthesised from F-class fly ash by the hydrothermal method [1], while the zeolite-carbon composite was produced from high-carbon fly ash (HCFA) via a single-step hydrothermal conversion process [2]. Two pesticides were chosen for the experiments: simazine (6-chloro-2-N,4-N-diethyl-1,3,5-triazine-2,4-diamine) and carbendazim (methyl N-(1H-benzimidazol-2-yl)carbamate). The tests involve the influence of the initial concentration (0.25, 0.5, 1.0, 2.0, and 4.0 mg/l), the initial pH value of the pesticide solution (3, 5, 7, and 9), and the kinetics of adsorption. Moreover, chemical regeneration with the use of ethanol was performed. The concentration of each pesticide in water samples was analysed using a Knauer high-performance liquid chromatography with a UV detector K-2600. The experiment on the influence of the initial pH of pesticide solution on the adsorption revealed that the adsorption of carbendazim on zeolite-carbon composite is the most effective and reaches almost 80%, while for zeolites is below 35%. For both samples, there is a slight elevation in adsorption depending on the pH; however, pH 5 and 7 appear to be the most favourable for the adsorption of carbendazim. The adsorption of simazine is also the highest (~90%) for the zeolite-carbon composite regardless of the pH. The results of the experiment performed to determine the effect of the initial concentration on the sorption of pesticides clearly show that an increase in the concentration of sorbate in the solution is associated with an increase in the sorption capacity. This correlation was observed for both adsorbents. The maximum adsorption capacity was not achieved for any adsorbent as the flattening was not reached. Pesticides are compounds hardly soluble in water; therefore, the possibility of preparing a solution with a higher initial concentration was limited. Moreover, the adsorption of pesticides on zeolite-carbon composite is a speedy process. During the first 30 s of the adsorption time, up to 90% of pesticides are adsorbed, and equilibrium is reached in less than 10 min. The analysis of chemical regeneration showed that effective regeneration and reuse of the adsorbent are possible. During the four cycles of adsorption-regeneration, the high adsorption abilities are maintained.

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1150 - SIMPLE PREPARATION OF AMORPHOUS ALUMINOSILICATES AS EFFICIENT ION EXCHANGERS FOR AMMONIUM CATIONS FROM AQUEOUS SOLUTIONS

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High concentration of nitrogenous compounds, as ammonium cation, could lead to environmental problems, such as toxic algal blooms, fish kills and poor drinking water quality via eutrophication. Several techniques have been applied to remove ammonium cations from water flow, for instance air stripping, oxidation, precipitation, adsorption and biological treatments.[1] Ammonium recovery by ion-exchange shows several advantages as high removal efficiency, low energy consumption and ease of operation. Natural zeolites like clinoptilolite are widely used as ion exchangers, but their exchange capacities are usually low.[2] On the other hand, synthetic zeolites show high ion-exchange capacity and selectivity, but a higher cost of production. Recently, the preparation of amorphous aluminosilicates by a co-precipitation method has been reported by our group.[3] Despite of the amorphous XRD patterns, the solids showed high ion-exchange capacity. In this work, amorphous aluminosilicates of different aluminium contents were prepared and evaluated as ion exchangers for removal of ammonium cations from aqueous solutions.

Preparation of the solids: Synthetic mordenite and natural zeolite were provided by Tosoh Corporation and Zeeklite Company, respectively. Amorphous aluminosilicates were prepared by a co-precipitation method based on previously reported procedures.[4] A basic sodium silicate solution was mixed with an acid aluminium sulphate solution under room temperature and neutral pH. The precipitate was recovered by filtration, washed with deionized water and dried at 80°C. The obtained solids were named as CP (co-precipitated) followed by a number which indicated the Si/Al ratio of the solids (CP-1, CP-3, CP-5).

Ammonium removal experiments: A required amount of solid was added to model NH4Cl solutions of different concentrations prepared by dissolving NH4Cl (Wako) in distilled water. The suspensions were kept under stirring at room temperature for different periods. The solid was separated by filtration and the liquid was analysed to determine the ammonium concentration.

Synthetic mordenite presents the characteristic diffraction peaks of the MOR phase with high crystallinity in the XRD pattern, while the natural zeolite shows the mixture of low crystalline mordenite and clinoptilolite (MOR and HEU structures, respectively). The amorphous nature of the solids CP-1, CP-3, CP-5 was confirmed by the presence of a broad diffraction peak $2\theta = 20 - 30°$, while AO-3 solid presents a mixture of amorphous matter and Na2SO4 associated with the presence of some solid residue that was not washed well during the preparation of the solid. All CP samples showed higher ammonium removal efficiency and ion exchange capacities than both zeolites whereas the ammonium uptake increases with the Al content of the CP samples. CP-1 showed the highest ammonium uptake (35.4 mg g-1) which is more than 3 times higher than the value obtained with the clinoptilolite while keeping high removal efficiency. The simple and flexible preparation of these amorphous aluminosilicates combined with their high ammonium exchange capacity suggests promising applications of these materials as ion exchangers for ammonium removal from wastewater.

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1214 - INVESTIGATIONS OF CO NO AND WATER ADSORPTION ON NICKEL FAUJASITES TO TREAT THE EXHAUST GAS DIESEL DFT SYNTHESIS AND ADSORPTIONS

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This article evaluates the adsorption capacity of NO, CO and water and their competitive behaviour on faujasite NaY (Si/Al=2.55) and NaX (Si/Al=1.23) exchanged with the nickel cation. This work is in keeping with the occupational health and more specifically the treatment of diesel exhaust gas in confined work environments. Remove these pollutants requires to find a selective material which can adsorb of NO and CO in the presence of water. Nickel transition metal has been chosen thanks to molecular modelling: DFT calculations. Indeed, the structures of the involving adsorption of CO, NO and water on the over NiY, NiX, NaY and NaX have been calculated investigated with the GGA, PBE GGA method with D2 dispersion correction scheme method [1], [2]. A screening has been performed on divalent cations and interaction energy of each gas on the four zeolites have been obtain Whatever the Si/Al ratio, the adsorption energy calculations show that sodium exhibit a higher affinity for water than NO and CO, indicating its unsuitability for the treatment of exhaust gas diesel. Ni cation behaves more efficiently, since each faujasites, NiX and NiY, show a greater affinity for NO and CO than with water.

The cation-exchange was then performed by treating the two zeolites with nickel salt solution [3]. ICP OES and XRD analysis, carried out on the solid phase, allowed to observe an over-exchange due to the presence of nickel hydrated into the salt solution. Nevertheless a mass balance performed on sodium cation demonstrated that the cation-exchange was successfully [4]. The manometry (Belsorp max II apparatus - BEL company), and thermogravimetry technics (Setys Setaram) were used to provide adsorption isotherms of CO, NO and water with sodium and nickel exchanged faujasites. Experiments carried out at least three temperatures (5, 25 and 35°C) to obtain the adsorption enthalpy of all gas by the isoster method. The textural properties were obtained by nitrogen adsorption/desorption experiments carried out at 77 K. These investigations allowed showing that the crystal structure has not been damaged by the multiple exchanges carried out.

This work allowed validating DFT calculations, to determine equilibrium constant and to assess the adsorbed amount maximum of gas. Whatever temperature, all adsorption capacities of NO and CO increased with the presence of nickel. The cationic exchange has not a significant influence on the water adsorption. Its adsorption capacity keeps the same order of magnitude after comparison between NaY/NiY and NaX/NiX but it remained very high for X-faujasite: X-faujasites were moderately selectivity for water. Hence, the gap of adsorbed amount between pollutants and water increases clearly from NaY to NiY. Dynamic experiments revealed and confirmed this last remark and the interest of nickel cation. They pinpointed too the influence of the breakthrough shape and consequently the Si/Al ratio on the resistance of the mass transfer. The zeolite studied indicated that the NiY zeolite performs the three other materials and revealed that cation nickel is the most appropriate divalent cations to selectively trap the NO and CO molecules in the presence of water.

1243 - TRANSITION METAL OXIDES SUPPORTED ON ZEOLITE DECORATED CERAMIC MONOLITHS PREPARED BY 3D PRINTING TECHNIQUE FOR CATALYTIC COMBUSTION OF VOLATILE ORGANIC COMPOUNDS

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Volatile organic compounds (VOCs) belong to a wide group of air pollutants that can cause a variety of harmful effects to the environment and human health [1]. Catalytic combustion seems to be one of the most promising destructive techniques for the removal of VOCs, which allow their conversion to less burdensome or environmentally benign products. Usually studied catalysts containing noble metals (e.g. Pt, Pd) show very high activity, but are characterized by high production costs and are easily deactivated in the presence of halogen-containing compounds. Thus, catalysts based on transition metal oxides appear as a sensible alternative. As demonstrated, generating the catalytic activity of such systems is strongly influenced by a high dispersion of active phase and its availability for reacting VOCs molecules, which sometimes occur in low concentration in air streams at high volumetric flow rates. For such purposes, we have undertaken research on monolithic catalysts with framework produced by the templating technique with the use of matrices obtained by 3D printing.

The 3D printed resin-based template was modified with a paste consisting of α-Al_2O_3 powder dispersed in a sodium silicate solution and calcined at 850 °C [2,3]. Subsequently, the walls of the resulting monolith were coated with a MFI zeolite layer to enhance their porosity. Finally, various amounts of precursors of the active phase (single Co, Cu, and Mn oxides as well as their mixtures) were introduced by wet impregnation. The produced materials were characterized by XRD (structure), low-temperature N_2 adsorption (texture), SEM (morphology), XRF (chemical composition), UV-Vis-DR (active phase state), XPS (surface composition), NH_3-TPD (acidity) and H_2-TPR (reducibility), and tested as catalysts in the total oxidation of toluene under various conditions.

The best catalytic results were obtained for the monoliths containing individual CuO or Co_3O_4 oxides, as well as for the Cu-Mn-O systems. The catalytic activity was correlated to mobility of the lattice oxygen involved in the oxidation process following the Mars–van Krevelen mechanism. The high-silica zeolite washcoat ensured a low concentration of surface acid sites, inhibiting the cracking reactions, hence very high selectivity towards CO_2 was achieved under the process conditions. Furthermore, we found relationship between the type of active phase and its behaviour in long-term stability tests, which was attributed to appearance of temperature gradient along a monolith piece due to exothermic effect of the toluene combustion. The measurements showed that in selected cases, the temperature difference between the ends of monolith (with length of 4.7 cm) reached even 100 °C favouring the aggregation of active phase nanoparticles. This drawback was eliminated by replacing one piece of monolith with a cascade of 3-4 shorter, strictly fitted monoliths. Many different arrangements of short monoliths (various order of monoliths with different composition of the active phase and its content) were tested.

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1271 - INFLUENCE OF PBT DIAMETER ON COPPER SORPTION ON ZEOLITE NAX IN BAFFLED BATCH REACTOR

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Sorption is a practical process for removing various pollutants from wastewater that is affected by variables such as initial concentrations, temperature, pH, coexisting ions, and mixing, all of which must be known for appropriate reactor design. If sorption is performed in a batch reactor, a suitable mixing speed must be ensured to completely suspend the sorbent, since below this mixing speed, the entire surface area of the sorbent is not available for sorption and above it, the sorption rate increases slowly or not at all with the intensity of agitation [1]. This can be achieved by optimising the hydrodynamic conditions, i.e., by providing sufficient agitation to suspend all particles and prevent their accumulation at the reactor bottom. These conditions can be classified as "just-suspended", NJS [2]. The variables affecting the minimum rotational speed required to achieve NJS has generated considerable research interest. NJS has been found to be affected by several variables, including solid concentration, particle density, and mean particle diameter, as well as hydrodynamic conditions in the reactor, which are influenced by the reactor and impeller configuration [3-5]. In this work, hydrodynamic conditions generated by pitched blade turbine (PBT) impellers on zeolite particles suspension in the batch reactor with baffles were investigated. The objective of this work was to analyse influence of impeller diameter NJS, maximum amount of copper sorbed onto zeolite NaX and copper sorption kinetics.

The experiments were performed in an uncovered baffled batch glass reactor with constant initial solution concentration (12.067 mmol/dm3), temperature (298 K), volume (2.14 dm3) and zeolite mass (15.75 g). The zeolite NaX particles used in the experiments were smaller than 0.09 mm. The suspension height corresponded to the inner batch reactor diameter. Nonstandard impeller off-bottom clearance, 0.1, was used. Stirring was performed using a PBT with four blades. Impeller to tank diameter ratio (D/dT) was varied in the range from 0.32 – 0.68. All kinetic experiments were performed at impeller speed which ensured the state of complete suspension determined by Zwietering's visual method [3]. The Mixed surface reaction and diffusion-controlled sorption kinetic model and Ritchie's model were used for the kinetic analysis of the obtained experimental kinetic data [6]. Valuable insight into the complex flow kinetics was obtained from a developed transient multiphase computational fluid dynamics model using the commercial software ANSYS Fluent v17.2.

The NJS increased when the D/dT ratio studied decreased. Kinetic analysis of the obtained experimental data using selected kinetic models revealed that Ritchie's model describes the copper (II) ions sorption kinetics on zeolite NaX, i.e., the sorption process investigated is kinetic controlled, regardless the D/dT ratio. The process is fastest when the largest PBT impeller is used.

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1295 - HIERARCHICAL ZSM 5 BASED CATALYSTS FOR SIMULTANEOUS ABATEMENT OF CO AND NOX AT LOW TEMPERATURES

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Emission of NOx and CO is one of the major drawbacks of fossil fuel combustion, causing serious health and environmental issues on global, regional and local scale. Strict legislation is imposed worldwide in order to reduce their emission from flue gases; therefore the scientific community as well as the industry are forced to continuously improve depollution technologies. Among other proposed deNOx methods, selective catalytic reduction using NH3 (NH3-SCR) has been widely investigated and commercially implemented. Its effectiveness is dependent on the properties of the used catalyst, on the temperature and the composition of the flue gas, which, however, can contain components responsible for catalyst deactivation and poisoning. Namely, some catalysts exhibit high efficiency at >300 °C and have been applied in thermal power plants, but they suffer from drawbacks such as being deactivated by SO2, phosphorous or metallic species.

Up to now, there are no effective catalysts with the ability to accommodate the dual-reactions of NH3-SCR and CO oxidation in a satisfactory manner. The NH3-SCR reaction requires strong acidity and moderate oxidizing ability (too strong oxidizing ability will accelerate the direct oxidation of NH3 by O2); while the oxidation of CO requires strong oxidizing ability. Moreover, the existing catalysts are not suitable for applications with low temperature flue gas (<300 °C), what is very often necessary.

In this work, simultaneous removal of NOx and CO in the SCR deNOx and CO oxidation reactions was investigated using catalysts based on the hierarchical form of ZSM-5 zeolite which was obtained from parent microporous analogue subjected to NaOH treatment followed by mild acid treatment [1]. Hierarchical ZSM-5 was ion-exchanged with Fe, Cu, Ce and Mn. Fe/ZM, Cu/ZM, Ce/ZM, Mn/ZM, FeCu/ZM, FeCe/ZM, FeMn/ZM, CeCu/ZM, CuMn/ZM and CeMn/ZM were prepared (ZM means modified - hierarchical ZSM-5). Based on previous experience, catalytically favourable better dispersion of introduced metal species is expected on hierarchical form of zeolite ZSM-5. The state of cations was revealed by diffuse reflectance UV-Vis spectroscopy; the distribution of pore diameters, amount of external/mesoporous surface and cristallinity of parent and hierarchical zeolite ZSM-5, and of ion-exchanged forms, are probed by conventional low temperature nitrogen adsorption and XRD methods, respectively. The samples were catalytically tested [2] in order to investigate the individual influence of cations presence on the activity, as well as the effects of combining cations. All applied catalysts show significantly higher activity when used in separate reactions than when both processes are performed simultaneously, which is the reason why a satisfactory catalyst is still a great scientific challenge. It was noticed that the change in the composition of the reaction mixture affects the efficiency of the catalytic process, and that at certain concentrations, an increase in the efficiency of the catalyst is achieved even at lower temperatures. Up to now, among all the tested samples, the sample with a combination of Cu and Ce showed the best overall activity, as well as the best activity at lower temperatures. Further investigations will comprise the application of different hierarchical supports and the modification both of reaction conditions and the way of metallic ions introduction inside ZSM-5 structure.

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1319 - BEA ZEOLITE BASED TIO2 COMPOSITES FOR GAS PHASE ETHYLENE PHOTOOXIDATION

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Ethylene is a natural hormone for the maturation process of climacteric fruits and is released during the respiration of fruits. The maturation process decreases fruit shelf-life, increasing the waste production [1]. A efficient and cheap process consists of decomposing ethylene into CO2 and H2O in presence of a photocatalysts (i.e. a semiconductor and light photooxidation process). The most common semiconductor used in photocatalysis is TiO2, due to its high efficiency and low cost. However, the use of bulk TiO2 has a few drawbacks, such as a limited adsorption for reactants and products [2]. One way to overcome this limitation is to support TiO2 onto zeolites as they present high surface area and high adsorption capacity that allow to gather and easily concentrate reactants. In particular, BEA zeolite, a highly hydrophilic material with a high external surface area, seems to be a very good candidate to support TiO2 nanoparticles. TiO2/BEA composites (BEA supplied by Zeolyst with a Si/Al ratio of 12.5) were prepared by sol-gel method, using two different alcohol solvents (2-propanol and ethanol). The use of two different solvents allowed to obtain composites with slightly different features that impact on the ethylene photooxidation. For both solvents, composites with two different TiO2 concentrations were prepared (20 and 30 % wt.) and compared. DRS UV-Visible spectroscopy was performed and showed that all samples had absorption of light below 350 nm (Figure 1a). XRD characterization was also performed and revealed that TiO2 anatase phase was present in all samples. Ethylene photooxidation was performed with a fixed bed quartz reactor, loaded with 0.45 g of catalyst, and a gas mixture containing 100 ppm of C2H4, 5 % He, 45 % O2 and 50 % N2. Before every reaction the gas was let to pass in the reactor to reach the adsorption-desorption equilibrium (dark experiments). After that, the reactor was irradiated by a medium-pressure mercury lamp (125 W). The lamp is placed in a quartz or glass water cooling jacket, for experiments in UV-Vis or UVA-Vis range ($\lambda > 350$ nm), respectively. Ethylene photooxidation results show that: i) samples showed higher conversions under UV-Vis irradiation than under UVA-Vis irradiation, since TiO2 could absorb more light and generate more radicals, ii) samples prepared with ethanol had higher ethylene conversions than those prepared with 2-propanol (Figure 1b), probably because a higher dispersion of TiO2 particles in the zeolite matrix is obtained for method 2, and iii) sample with 30 % TiO2 (ethanol as solvent) reached 100 % ethylene degradation, converting all ethylene into CO2 and H2O UV-Vis experiments.

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1354 - TIO2 CQDS NANOCOMPOSITES FOR PHOTOCATALYTIC DEGRADATION OF DICLOFENAC

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Pharmaceutical and personal care products are considered emerging organic pollutants for sewage, surface and groundwater. Some of these compounds, including diclofenac (2-[2’, 6’-(dichlorophenil)amino]phenilacetic acid), a non-steroidal anti-inflammatory drugs (NSAID) frequently used to treat inflammation and pain associated with different rheumatic and non-rheumatic diseases, has been found in many environmental samples such as wastewater, surface and drinking water. Such compounds could actually cause ecologically harmful effects, such as endocrine disruption and antimicrobial resistance [1]. Moreover, the presence of diclofenac in drinking water lead to severe adverse effects even at low concentrations [2], like cytotoxicity to liver, kidney and gill cells, as well as renal lesions.

To date, various semiconductors were used in photocatalytic degradations, but undoubted, titanium dioxide (TiO2) is one of the most widely studied due to its abundance, low cost, low toxicity, superior photostability, and high intrinsic catalytic activity under UV illumination. However, in spite of all these advantages, the poor responses to visible light caused by its wide bandgap (3.0–3.2eV) and the fast recombination of photogenerated electron-hole pairs had significantly hindered its application in photocatalysis [3]. As to improve the photocatalytic properties of the TiO2 a combination with carbon structures was investigated. Particularly, CQDs were used to address the problem of the wide bandgap. The induced modifications are controlled by the CQDs dimensions [4].

In this work, TiO2-CQDs nanocomposites were used as photocatalysts for the degradation of diclofenac under UV and Vis irradiation. CQDs, prepared by a friendly low-temperature hydrothermal decomposition of humins wastes (i.e., insoluble polyfuranic polymers by-products generated from D-glucose acid-catalyzed dehydration [5]), were dispersed in the TiO2 matrix because of their synergistic effects, which lead to a reinforced photocatalytic performance. The mechanism of degradation of aqueous diclofenac by TiO2-CQD nanoheteroconjunctions was investigated, as well as the influence of the type and load of catalyst, type of irradiation source and influence of the addition of H2O2.

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1369 - SYNTHESIS OF CU CHA ZEOLITES AND EVALUATION OF THEIR CATALYTIC PERFORMANCE IN C3H6 NO SCR REACTION

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Nitrogen oxides NO and NO2 are the main cause for the formation of acid rain and photochemical smog, whereas N2O contributes to global warming and the depletion of the ozone layer. Thus, the removal of nitrogen oxides (NOx) from emissions via catalytic conversion to N2 is an important process in environmental catalysis. There are currently two main alternative routes used for selective catalytic NOx reduction in oxygen rich exhausts: with ammonia, or hydrocarbons as reducing agent.

Former studies showed that copper zeolite catalysts perform well in the selective catalytic reduction of NOx by propene (C3H6/NOx-SCR) [1], but further development is required to improve their stability and low-temperature activity. The development of a catalyst with high activity, good selectivity, appropriate (hydro)thermal stability in a broad temperature window requires precise control of its properties [2]. Detailed knowledge of the synthesis and post synthesis pathways taking place in the course of the catalyst preparation allows engineering of a material having pre-determined properties [3]. It was also demonstrated that the nuclearity of the active copper site is closely related to the preparation method of the zeolite [4]. Special attention was devoted to understanding of the features of zeolite supports synthesized in the presence of different alkali cations (Na+, K+) in the reaction mixture.

In this study, chabazite type SSZ-13 zeolite samples (Si/AlF=11 and 14) were prepared by hydrothermal synthesis using N,N,N-trimethyladamantammonium hydroxide as organic structure directing agent. For the sake of comparison, commercially available SSZ-13 (ACS Materials) was also used. To incorporate catalytically active copper centres, the zeolite samples were first ion-exchanged into the NH4-form followed by mechanochemically assisted ion-exchange using copper nitrate or copper acetate salt. The potential application of thus obtained Cu-SSZ-13 catalysts for C3H6/NOx-SCR was evaluated in the temperature range of 150-550 °C. The crystalline phase and chemical composition, as well as morphology and surface hydroxyl groups of the catalysts were determined on the grounds of XRPD, ICP, SEM and FTIR analyses, respectively. Copper species were characterized by temperature programmed reduction with hydrogen and carbon monoxide (H2-TPR and CO-TPR), and via chemisorption of carbon monoxide followed by FTIR. High copper

content (3-10 wt. %) was achieved with all three zeolite samples while formation of copper oxide phase was not detectable by XRPD. At 300 °C significantly higher N2 yield was observed over the catalysts prepared with controlled zeolite synthesis compared to the catalysts prepared from the commercial SSZ-13 zeolite. The collected set of data demonstrates that the conditions of the process of zeolite synthesis and copper introduction play a determining role in the improvement of the catalytic activity.

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1352 - THE POTENTIAL FOR BIOAUGMENTATION OF WASTEWATER TREATMENT PLANTS BY BIOPARTICLES MADE OF NATURAL ZEOLITE

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This study investigated how bioparticles can withstand extreme environmental conditions commonly found in wastewater treatment systems, including pH fluctuations, the influence of toxicants, and grazing by protozoa. In this case, the bioparticles refer to particles consisting of natural zeolitized tuff with a biofilm of Acinetobacter junii, a phosphate-accumulating bacterial species, on their surface. The idea was that the bacteria would form a compact biofilm at the zeolite surface and be protected from harmful environmental conditions by the self-produced exopolymeric substance layer.

The particles, sieved to 0.125 – 0.25 mm size fraction, were obtained from natural zeolite (NZ) bedrock from Bigadic in Turkey. As estimated by the X-ray powder diffraction method, the NZ sample consisted of 70 % clinoptilolite, subordinate opal-CT, and quartz, 10–15% each, and traces of K-feldspar and mica [1]. The used bacterium, A. junii, is classified as a phosphate-accumulating organism, meaning it can accumulate more phosphate in its cell than necessary for its primary metabolism. This strain was initially isolated from a wastewater treatment plant with EBPR characteristics (Enhanced Biological Phosphorus Removal) and obtained from a bank of microorganisms for this research.

The results showed that the bacteria formed an abundant biofilm on the particle surface with numbers of immobilized bacteria reaching up to 5×109 cells per gram of NZ. The biofilm could resist the adverse effects of acidic pH, high concentrations of commonly used disinfectant benzalkonium-chloride (BAC), and grazing by protozoa Paramecium caudatum and Euplotes affinis, even when planktonic bacteria were eradicated under the same conditions.

In initial experiments, the ideal pH value for A. junii growth in a liquid medium was shown to be at 7, higher pH up to 10 showed no significant negative effect, but values below 6 had a strong bactericidal effect. At pH 4, all the bacteria were destroyed. However, in the form of bioparticles, in a liquid medium at pH 4, bacterial survival was 87, and even at pH 3, almost 50 %.

A similar protective effect was observed in a liquid medium with BAC. While all bacterial cells were destroyed at BAC concentrations of 50 mg/L, the decay of bacteria from the bioparticles was only 12 %. When bioparticles were added to the experimental setup containing grazing protozoa in liquid media, again, the number of bacteria after 24 h was significantly higher when compared to the bacteria added as planktonic culture.

Not only did the bioparticles provide protection in the form of biofilm, but during 24 h of incubation, the bacterial cells were detaching from the surface of the NZ and enriching the surrounding bulk liquid. Such observations suggested that biofilms formed on the NZ surface could be the source for successful bioaugmentation of wastewater.

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1044 - AB INITIO SCREENING OF DIVALENT CATIONS EMBEDDED IN CHABAZITE FOR SEPARATION OPERATIONS INVOLVING CH4 CO2 H2 AND N2

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The optimization of separation and adsorption processes such as purification of CH4 rich mixture (biogas or natural gas), CO2 capture technologies (CCS) or the valorization of H2 is urgently needed to meet the key energetic and environmental transitions. In particular, accurate knowledge regarding the selectivity of selected binary or ternary important separations, e.g., CO2/CH4 or N2/CO2 or H2/N2 separations, is crucial to improve the current technological state-of-the-art. In this contribution, we focus on chabazite (CHA), a small pore zeolite (8-membered ring (8MR) windows) used in numerous industrial applications correlated with separation, adsorption, and catalysis.[2,3] So far, most of the studies dealt with monovalent cations exchanged chabazites.[2] Herein, we present the results of a systematic computational screening (i.e., periodic DFT calculations with TS/HI dispersion correction, as implemented in VASP code)[4] of a series of divalent cations, selected among the cheapest and readily available metal divalent cations (Ca2+, Mg2+, Fe2+, Cu2+, Zn2+, Sn2+).[5] The two most stable sites (SII sites, 6MR) followed by the two most stable SIV sites (8MR) and the small SIII site (4MR) (see Fig 1.a). Due to reported impossible/severely limited accessibility of SI sites originating from structure steric hindrance, this site was ignored. Our data revealed that Mg-CHA (Si/Al = 11, 100% exchanged) is the most promising combination for CO2/CH4 separation (Fig 1.b). To complement this static investigation at T = 0 K in more relevant operation conditions, ab initio molecular dynamics simulations at finite temperature (AIMD, T = 300 K) were performed: the calculation of adsorption enthalpies of CO2 and CH4 and the investigation of co-adsorption of CO2 in presence of an excess of CH4 has confirmed the potential interest of this material. For the purification of H2 rich mixture, some divalent cation exchanged CHA must be discarded because of dissociative adsorption preventing regeneration of the material and of H2(g). In light of these results, Ca-CHA appears as a promising candidate for H2/N2 separation. Finally, Ca and Mg-CHA were also found to be the best materials for the removal of CO2 from N2 rich mixtures. Further AIMD and experimental work is ongoing to fully harness these findings and extend them to other important zeolitic structures.

Fig. 1. a) Extra-framework cation binding sites SI to SIV. b) Difference of adsorption energies of CO2 and CH4 on the series of divalent cation exchanged CHA.

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1056 - ZEOLITES FOR BIOMASS TRANSFORMATION PROBING THE DYNAMICS AND ADSORPTION OF LIGNIN DERIVED CRESOL ISOMERS WITHIN ZEOLITES

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A promising alternative renewable feedstock to crude oil for fuel and chemicals is lignin - an abundant component of lignocellulosic biomass comprising 40% of its energy. Zeolite catalysts will be of great importance for lignin depolymerisation and upgrading, not least due to their commercial use in the petrochemical industry, where mixed feeds of biomass and crude oil have already been employed [1]. Their versatile framework topologies and acid site densities also offer reactant and product selectivity and fine control of the catalytic process.

Methylphenol isomers (cresols) constitute some of the simplest derivatives obtained from lignin depolymerisation and thus have been implemented in many catalytic studies as a model lignin molecule [2-3]. They are vital precursors for manufacturing dyes, agrochemicals, pharmaceuticals, polymers and BTX (benzene, toluene, and xylene) fuels. Studies of rate limiting processes involved in lignin conversion, including diffusion throughout the zeolite framework and adsorption onto the acid sites, are scarce in the literature. Quasielastic (QENS) and inelastic (INS) neutron scattering are uniquely powerful experimental techniques for studying diffusion and adsorption respectively [4].

Here, tandem QENS and molecular dynamics (MD) experiments have been employed to study cresol mobility within highly Brønsted acidic zeolites as a function of isomer-type (meta and para-cresol) and zeolite type (H-Y and H-beta), from 340 – 400 K. Initially, bulk liquid cresol diffusion was investigated where both jump diffusion and local rotational motions were observed and different computational models were evaluated upon their ability to reproduce cresol dynamics. Upon dosing the cresol isomers into the zeolite systems, only localised isotropic rotational dynamics were observed over the timescale of the instrument at rates of 3.03 – 5.11 × 1010 s-1, which was slower than the rotation of cresol molecules within a liquid (5.7 – 9.2 × 1010 s-1). A greater population of mobile cresol (by an average factor of 2.3) was observed in the larger pores of zeolite H-Y (7.4 Å and 13 Å in diameter) compared to the pores of H-Beta (6.7 Å in diameter), with activation energies for rotation from 4.2 – 6.6 kJmol-1. The linear para-cresol displayed an average factor of 1.2 more molecules rotating compared to meta-cresol. However, by accessing longer timescales across several nanoseconds using MD simulations translational diffusion was observed alongside rotation but at a slower rate compared to the translational diffusion coefficients calculated from simulations of bulk liquid cresol [5].

Equally essential to the catalytic process are cresol-acid site interactions. INS was used to probed said interaction strengths by analysing changes in the vibrational frequencies of the cresol molecules. The shifting and diminishing of peaks relating to the hydroxyl bending of the cresol (~350 cm-1) when inside the zeolite indicates the occurrence of hydroxyl adsorption interactions with the zeolite Brønsted acid site. More complex density functional theory calculations have enabled further analysis of cresol interactions with the zeolite framework.

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1077 - THE EFFECT OF DIFFERENT SI AL RATIOS ON THE RELEASE RATE OF ANTI CANCER DRUG 5 FLUOROURACIL FROM ZEOLITE BETA.

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Anti-cancer drugs, for example 5-Fluorouracil, typically experience issues with dosages and bioavailability. Often, administered dosages are larger than required, according to the drugs therapeutic window, to achieve a successful impact of the drug on the cancer after accounting for poor absorbance and specificity. This in turn increases the occurrence and severity of observed side effects. Zeolites are promising materials for drug delivery systems with the potential to increase bioavailability of anti-cancer drugs, maintain their therapeutic range for prolonged periods, and therefore mitigate severe side effects with potentiated drug effect, without inducing side effects of their own. [1],[2]

Dynamical behaviour of 5-Fluorouracil encapsulated within the pores of zeolites can be affected by numerous variables. Most notably, pore size and topology can influence and restrict diffusion, and silicon to aluminium ratio can influence diffusivity,[3] via an affinity of some organic functional groups to bind with the Brønsted -acidic sites in systems with aluminium presence. Defining the relationship between the molecular-scale dynamics and release profile of a drug from a zeolite may provide insight into a systematic procedure whereby release for any drug candidate can be predicted and tuned via utilisation of molecular dynamics simulations.

The controlled release of 5-Fluorouracil was studied as a function of zeolite composition (Si/Al ratio = 19 and 180). A factor of ~1.5 more 5-FU was released from the sample with Si/Al ratio = 180 (H-BEA) over the release period, indicating that the system with fewer strongly absorbing Brønsted acid sites released the drug more rapidly. Thermogravimetric analysis results concluded that the loading capacity of H-BEA was a factor of ~1.5 greater than the sample with Si/Al = 19 (BEA), thus the increased release rate may be attributed to this result. Quasielastic neutron scattering (QENS) studies showed that most of the confined drug was immobile on the ~500 ps timescale probed by the instrument in both samples. The H-Beta sample showed 4% of the molecules were diffusing in a sphere of dimensions matching the zeolite Beta intersections, and 6% of the molecules were carrying out this same motion in BEA.

The studies suggest that steric hindrance caused by molecule-molecule interactions in the constrictive zeolite pore system is the significant factor in adsorbed drug behaviour, and that the degree of loading remains the most significant factor in release rate. Molecular dynamics simulations which probed the effect of both acid site concentration and drug loading, showed that this 'confined diffusion' decreased in magnitude with both Si/Al ratio and lower molecular loading, but that the loading was the dominant factor. The study shows the complex relationship between zeolite composition, drug loading, molecular behaviour, and release rate in the design of controlled release systems for anticancer drug delivery.

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1095 - MOLECULAR SIMULATION OF AQUEOUS ELECTROLYTE SOLUTION INSERTION IN ZEOSILS IN THE OSMOTIC ENSEMBLE

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Molecular simulations involving adsorption of electrolyte solutions in porous materials are usually performed at a fixed amount of salt ions in the system, reproducing macroscopic concentration. [1] Although this statement is valid in the bulk, the nanoporous material in equilibrium with the bulk electrolyte exchange water molecules and ions so that the concentration of an electrolyte confined in a nanoporous material is greatly affected and remains unknown. The Grand Canonical Monte Carlo (GCMC) simulation method is well-suited for simulating the molecular insertion or exchange of neutral species in fluid phases. However, its use for ionic species is particularly inefficient: in addition to the fact that finding suitable cavities large enough in the fluid to accomodate ion insertion would appear infrequently, the strong organization of the solvent induced by the electric charge gives the insertion move a low probability. Secondly, electrical neutrality of the system imposes the insertion of pairs of charge-balancing ions, which further decreases the probability of a successful Monte Carlo insertion move.

Therein, we propose an algorithm based on non-equilibrium candidate Monte Carlo (NCMC) moves to ultimately perform MC simulations in contact with a saline reservoir. [2] The NCMC move consists of choosing a pair of water molecules that are alchemically transformed to a salt pair (or vice versa) along a path consisting of an interpolation of the nonbonded parameters of water and ions followed by short MD relaxation steps. We adapt the Widom insertion technique to determine the chemical potential Δμ associated with the transmutation of water molecules to an ion pair by using NCMC moves. The chemical potential defines a Monte Carlo osmostat [3] in the semigrand constant volume and temperature ensemble (Δμ, N, V, T) to be added in a Monte Carlo simulation where the number of ions fluctuates. In order to validate the method, we adapted the NCMC move to determine the free energy of water solvation and subsequently explore thermodynamics of electrolyte solvation at infinite dilution in water. Finally, we implemented the osmostat in MC simulations initialized with bulk water that are driven towards electrolytes of similar concencentration as the saline reservoir.

We apply the osmostat to zeosils for which adsorption isotherm of pure TIP4P water has been determined with GCMC simulations. Depending of the work performed to solvate ions in the zeosils during NCMC moves, one predicts whether ions penetrate the porous materials. Then, by adapting the NCMC move to calculate water free energy and deduce subsequently water chemical potential in bulk electrolyte solutions as a function of pressure, we predict empirically the shift of intrusion pressure of electrolyte solutions in these materials.

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1101 - MACHINE LEARNING ACCELERATED SIMULATIONS OF PLATINUM NANOPARTICLES ON HYDROXYLATED SILICA SUPPORTS

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Small platinum nanoparticles as heterogenous catalysts play a crucial role in several industrial processes.[1–3] Enhancing the catalytic performance requires highly dispersed Pt particles that are resilient to agglomeration and sintering. Stabilization of such particles can be controlled to a large extent by the metal oxide support or by Pt particle encapsulation, e.g., in zeolites.[2,3] Theoretical investigations have already provided valuable insights into the stabilization and migration mechanism of zeolite-encapsulated and silica-supported Pt particles.[4,5] However, the realistic modelling of complex (defect-containing) zeolites and external (hydroxylated) zeolite surfaces with hundreds of atoms per unit cell are currently beyond reach of accurate simulations at the density functional theory (DFT) level at the time-scales relevant for particle migration and agglomeration.

We address this challenge by training (SchNet)[6] neural network potentials (NNP) which are capable of speeding up DFT quality simulations by several orders of magnitude.[7] First, we extended our DFT (meta-GGA level) database for siliceous zeolites[8] and Pt containing zeolites[9] with configurations that form an interpolation grid representing the relevant interactions of sub-nanometre Pt particles with hydroxylated silica. The dataset was generated using a structurally diverse subset from numerous ab initio MD runs including Pt particles (up to Pt30) in silanol-defect-containing zeolites, hydrogen containing Pt particles up to ~1 nm, and gaseous H2 on a Pt surface. The NNPs trained on the generated database retain DFT accuracy with energy root-mean-square errors of ~6 meV/atom, which is approximately the same accuracy of previously trained zeolite NNPs.[8,9] Thorough tests showed that the NNPs keep DFT accuracy even for systems not considered on the training set such as large Pt particles (up to Pt38) on silicatene and on an external MWW surface model. We then systematically investigated the free energy migration pathways of small Pt particles in CHA as a function of temperature and silanol defect concentration using biased dynamics. Such biased MD simulations at the NNP level allow a computationally efficient sampling of the free energy surface, particularly in combination with machine learned collective variables[10] using the pretrained atomic representations of our NNPs.

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1114 - HOW MACHINE LEARNING POTENTIALS AND MOLECULAR DYNAMICS (NNP MD) HELP IN NMR CHARACTERISATION OF ZEOLITES

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Nuclear magnetic resonance (NMR) spectroscopy is an excellent method for understanding the local structure of NMR active nuclei in porous materials to determine their structure and dynamics[1][2]. Theoretical NMR calculations have been used to interpret experimental NMR results in 29Si, 27Al and 19F NMR. However, current computational NMR methods for zeolite calculations use static models representing the zeolite at 0 K[3][4]. This limits the accuracy, because vibrational motion is not considered and the processes that zeolites are involved in do not occur at 0 K[5]. In addition, the interactions of zeolites with water or during catalysis are not static. One method to improve on the static picture is to run a molecular dynamics (MD) simulation and average the shielding values. The issue is that DFT-MD has a high computational cost for running longer MD simulations, hence the limitation to a few picoseconds, and a lack of reliable sampling.

Machine learning potentials (MLPs) parameterized on DFT datasets can overcome this problem, as there is a lower computational cost, which allows for longer MD times with DFT accuracy [6]. Recently, machine learning has been used for understanding and predicting NMR parameters in various materials [7]. In this work, the method involved using reactive MLPs in combination with MD to model the zeolite. Firstly, we apply MLPs to calculate long-term MD trajectories of 1 ns. Then we extract shieldings from a trained kernel ridge regression (KRR) model. Finally, the shielding is averaged over the trajectory to implicitly include dynamic effects because local motions are allowed due to thermal fluctuations.

This novel Machine learning potential molecular dynamics (MLP-MD) method was verified and shown to reproduce the shieldings of structures to within the DFT reference precision. Then, it was used to calculate the shielding for 29Si and 17O nuclei for various published zeolites and to compare them with experimental NMR data. The calculated average shielding shows agreement for 17O shielding for siliceous Ferrierite to within 2-3 ppm. Hence, this method is promising for accurately reproducing NMR spectra of different nuclei for various zeolite frameworks. Currently, more complex zeolite systems are being investigated, including hydrated aluminosilicate zeolites with a variety of charge-compensating cations.

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1124 - EASY AND FAST IDENTIFICATION OF CRYSTALLINE TOPOLOGIES WITH CRYSTALNETS.JL

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The topology of a material is the set of properties which can be extracted from the graph of its chemical bonds, called its net. In the case of crystalline frameworks, this net is periodic, each of its vertices representing an atom or a cluster of atoms. This simplified representation of a structure abstracts away the shape of the unit cell, the positions of the atoms within, as well as the chemical nature of each atom, in order to concentrate on the underlying organisation of its bond network.

The topology may be used to group together frameworks sharing the same net for classification purpose, or to detect duplicates in structure databases for instance. In the case of zeolites, the net is unambiguously defined as the graph of the T-atoms, bonded by oxygen bridges ; however, for other materials like MOFs, the choice of clustering of atoms may lead to different underlying nets. The full topological information is then retrieved by accessing the several nets resulting from these clusterings. Yet, identifying whether a net is known and retrieving its name among a database of known topologies requires solving a computationally difficult task, known as the graph canonization problem.

We present CrystalNets.jl [1], a new open-source software written in Julia for the identification of crystalline topologies. It can recognize any net registered in the Reticular Chemical Structure Resource (RCSR) [2], the EPINET project [3] as well as the known zeolites topologies, from inputs given as CIF or other crystallographic file formats, according to several clustering options. On top of a custom bond-guessing algorithm tailored for porous materials, it relies on a modified and improved implementation of the Systre [4] algorithm, which assigns to each net a provably unique key, called the topological genome. This approach guarantees its correctness, while performance was measured to be an order of magnitude better than Systre on average. We also checked that the identification results were consistent with those of the proprietary ToposPro [5] software in spite of the algorithmic differences. This makes CrystalNets.jl suitable for fast and reliable analysis of large databases of materials, which we tested on various kinds of material (zeolites, MOFs, aluminophosphates, etc.).

We also present our new website which allows using CrystalNets.jl without any installation or prerequisite, through an intuitive interface. This website includes a visualisation panel to easily check the validity of the detected nets, making it amenable to use by non-experts in topology for the topological identification of experimental structures for example.

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1125 - MODELING OF PROBE MOLECULE ADSORPTION AND SI VACANCY FORMATION IN YNU 2 ZEOLITE

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The YNU-2 zeolite, with MSE framework, has excellent selectivity and catalytic activity in phenol oxidation to hydroquinone [1]. Using DFT modeling we showed that the YNU-2 zeolite should contain large amount of silanol nest, due to the easy formation of Si vacancies. Based on our modeling we demonstrated that the substitution of Si ions by Ti and Al in different crystallographic T-atom positions are energetically favorable by 150 - 220 kJ/mol [2]. In addition, the formation of silanol nests, in the vicinity of Ti, leads to stabilization of the framework due to the relaxation of the local framework tension arrogant Ti ions.

Further, we also modeled the adsorption of probe molecules as pyridine and acetonitrile, at a Ti site of the zeolite which allows us to characterize the active sites in more detail. In addition, we calculated the corresponding characteristic vibrational frequencies. The calculated values for the pyridine and acetonitrile before and after adsorption in the zeolite pores show that the shift depends on the position of the Ti site at which the probe molecule is adsorbed. On the other hand, the presence of silanol nest does not affect the frequencies.

The non-dissociative and dissociative adsorption of an oxidation agent (as H2O2) at the Ti centers was also investigated. The non-dissociative adsorption of H2O2 is more stable (the binding energy of the adsorbate is -70 kJ/mol), while the stability of dissociated peroxide is lower by ~45 kJ/mol. Interestingly, the presence of silanol defect close to the Ti center facilitates dissociative adsorption. Thus, the process becomes by ~20 kJ/mol more favorable in comparison to the structure with an absence of silanol nest in the vicinity of the Ti center [2].

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1135 - APPROACHING ENZYMATIC CATALYSIS WITH ZEOLITES AN AB INITIO AND EXPERIMENTAL STUDY OF ALKYLAROMATICS COMPETING REACTIONS.

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Production of alkylaromatics is a crucial process in the modern chemical industry since they are well-established precursors for many important intermediates widely used in chemical and pharmaceutical industries. Ethylbenzene (EB) is one of the industrial alkylaromatics with a higher production capacity worldwide which is mostly consumed in the manufacture of polystyrene, styrene-acrylonitrile resin, and other products.1 Benzene alkylation with light olefins and alcohols catalysed by acid zeolites has been stablished as the main way of industrial production for alkylaromatics. The industrial alkylation process inevitably produces undesired polyalkylated byproducts with lower added value with diethylbenzene (DEB) being the most common one and a considerable amount of ethene. To improve EB selectivity, the current production of EB combines two reaction processes: alkylation of benzene with ethene then followed by EB separation and transalkylation of the polyethylated byproducts with benzene to increase the global yield of EB recycling the side products already obtained. In a prior work from the group, we demonstrated how the ab initio designed and synthesized zeolite catalyst (ITQ-27) optimizes location, density, and environment of acid sites to drive the reaction through the preselected and preferred bimolecular diaryl-mediated mechanism, instead of the alkyl transfer pathway, as demonstrated by a periodic DFT study of both reaction mechanisms and compared with MOR zeolite which is normally used in industry.2 However, if during transalkylation two DEB molecules form a diaryl intermediate, with a subtle difference of two ethyl groups with respect to the transalkylation diaryl intermediate, disproportionation of 2DEB ◊ EB + TEB occurs reducing the selectivity towards EB. To further improve the catalyst efficiency by suppressing the disproportionation of DEB while enhancing transalkylation, the zeolite structure should be able to recognize this subtle difference, approaching the level of molecular recognition of enzymes. In this work we use a combination of computational and experimental techniques to achieve this challenging goal. Starting with the selection of the most stable DEB+ and disproportionation diarylic intermediates then followed by a high-throughput screening of all zeolite structures potentially well-suited to stabilize diaryl intermediates. Then improving the accuracy of the thermodynamic and kinetic data by means of periodic DFT calculations, a set of 11 large pore zeolites with different microporous structure of channels and cavities is proposed, BEA, BEC, BOG, CON, FAU, ITT, IWR, IWV, MOR, SEW, USI, UTL. From these calculations a parameter with the binding energies (BE) of the diaryl intermediates for disproportionation and transalkylation was established as a predictor for the selectivity towards TEB or EB. As this parameter showed disparity of values for similar 12-ring channel zeolites, a comprehensive periodic DFT mechanistic study for the four possible diaryl-mediated pathways was carried on for BEC, BOG, IWV, IWR, UTL and MOR discerning all features found for the different topologies and identifying the lowest energy path for each material. Finally, the synthesis, characterization and catalytic test of these materials confirms the theoretical predictions by a good correlation with experimental and theoretical activation energies for the complete list of catalysts and demonstrates that subtle changes in pore size and architecture can tune the preferred reaction pathways, leading to a precise control of the host-guest interactions that approaches the specificity of enzymatic catalysts. It also supports the proposal that the use of OSDAs that mimic the transition state of a given reaction can drive into zeolites well adapted to catalyze the reaction following and enzymatic way of catalysis.

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1136 - INCORPORATION OF TI IN SI FORM AND AL SI FORM OF YNU 5 ZEOLITE DFT STUDY

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YNU-5 zeolite with a YFI-type framework has 12-12-8-ring system, and isolated 8-ring channels separated from the system by a thin (mono-atomic silicate) wall. A combined IR analysis with the help of Density Functional Theory calculations show presence of Lewis acid sites. The agreement between the numbers of Brønsted acid sites and Al atoms was observed, and it was hypothesized that the Lewis acid sites are available, due to the bridging Si(OH)Al group in the YFI framework. The bridging OH groups were identified to be mainly at the isolated 8-membered rings. In addition, the dealumination at a high temperature under the reflux conditions with nitric acid led to the stabilization through migration of Si to the silanol nest, resulting in the preferential removal of Brønsted acid sites from the 12-12-8-ring system. This explains well the reported catalytic properties of YNU-5 zeolite for dimethyl ether-to-olefin reaction.
In order to increase the ability of the 12-12-8-ring system of YNU-5 zeolite for other catalytic reactions, additional fictionalization is needed. In the present study, the Density Functional Theory was used to examine the isomorphous substitution of Si by Ti ions in various T-sites in YNU-5 zeolite. We used PBE XC-functional with D3 empirical correction for the dispersion interactions. First, the isomorphous substitution of Si by Ti was evaluated for all T1-T9 positions in the pure Si-form of YNU-5. As a next step, the position of Ti in presence of Al in its most stable positions was also calculated.

The isomorphous substitution of Si by Ti was evaluated in the following formal reaction:
Si120O240 +Ti(OH)4 -> Si119TiO240 + Si(OH)4.
According to the above mentioned formal reaction, the substitution of Si by Ti is endothermic process with energy ranging from +150 to +167 kJ/mol. The energy for the substitution of Si by Ti in alumosilicate form of YNU-5 was evaluated in the following formal reaction: Zeo[(SiO2)116 (AlO2H)4]] + Ti(OH)4 → Zeo[(SiO2)115(AlO2H)4(TiO2)] + Si(OH)4, for YNU-5 zeolite with Al in T1, T4, and T5 positions, respectively. It was shown in previous study that these are the most populated T-sites with Al in YNU-5 zeolite [1]. There is no clear trend for the position of Ti with respect to the Al center in YNU-5. The relative stability of the different forms of YNU-5 zeolite shows that if the Al is in T1 and T4, the Ti prefers closer position with respect to Al-sites, and if the Al is in T5 position the Ti prefer to occupy distant T-sites. However the energy differences are not substantial, up to 30 kJ/mol.

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1160 - ANISOLE DISPROPORTIONATION OVER HZSM 5 ZEOLITES ASSESSING THE IMPACT OF SI AL RATIO ON POISONING THROUGH KINETIC MODELING AND DFT CALCULATIONS

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As the global economy is slowly shifting away from petroleum as a hydrocarbon source, new resources need to be found and exploited in order to fulfil the growing demand for transportation fuels, packaging plastics, digital devices, medical equipment, tires, etc. One such source is the aromatics family, which can be obtained from the Catalytic Fast Pyrolysis of biomass ("green" wastes, such as pine wood and bark, and lignocellulosic biomass in general). These BTX (Benzene, Toluene, Xylene) are high value chemicals, currently mainly produced from catalytic reforming, as well as FCC units in regular fuel refineries.

CFP of biomass offers an interesting route for the production of green hydrocarbons, by imitating the FCC process[1,2]. Pyrolysis happens in a dual fluidized bed, with a zeolite catalyst providing the deoxygenation to BTXs and olefins. However, there is also formation of coke and gas (CO, CO2), with the former participating to the deactivation of the catalyst, which remains the biggest technological lock preventing the commercialization of the technologies from Anellotech/Axens, BioBTX or RTI international. Thus, the investigation and comprehension of the catalyst's stability and deactivation process are paramount for this process' large scale exploitation.

Primary pyrolysis gases have an abundance of MeO-containing compounds, such as guaiacol, syringol, and their derivatives. Studying the behaviour of this methoxy group should provide insights on these primary pyrolysis products. Anisole is thus chosen as a model molecule, due to its relative simplicity (monoaromatic, one functional group), and its methoxy group. Finally, HZSM-5 has shown promise as a CFP catalyst, notably for its increased selectivity to aromatics.

The transformation of anisole was carried out over H-ZSM-5 (9<Si/Al<201) catalyst at 400 °C under 1 atm and partial anisole pressure of ≈0.048 atm. Experiments were performed at contact times (Wcata/FAnisole) ranging from 0.02 to 0.17 gcata.h.gAnisole-1 to evaluate activities and kinetics. Initial turnover frequencies (TOF0, nAnisole.nAcid sites-1.h-1) are assessed for each Si/Al ratio, and adsorption energies are calculated via DFT for anisole and its reaction products, comparing monomers and dimers, increasingly methylated derivatives, as well as showcasing the effect of the presence of a second acid site in proximity[3,4]. These conditions allow for the complete overview of the effect of Si/Al ratio (and therefore acid site density) on products retention and "coke" formation.

While drawing |-ln(1-X0)| vs W/F, one can first observe that anisole transformation on H-ZSM-5 follows an apparent first order reaction rate. With the activities extracted from, the TOF0 of each catalyst's acid sites can be deduced. Higher Si/Al ratios exhibit a much higher TOF0 than the lower ones, evidencing the superior activity of isolated (and stronger) Brønsted acid sites, in comparison to the paired, weaker ones of the lower Si/Al ratio. DFT calculations support this, showing the increase in adsorption energy for the adsorption of reaction products (Phenol, Cresol, etc.) on the catalyst's paired acid sites.

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1171 - INFLUENCE OF THE WATER LOADING RATIO ON THE DIFFUSION OF HTO RADIOLYSIS PRODUCTS H2 O2 AND H2O2 IN Z4A

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When tritiated water is stored in containers containing zeolite 4A pellets as adsorbate, the production of gaseous species H2 and O2 induced by self-radiolysis displays a complex behavior [1]. In a first stage, it is accelerated compared to the production rate in free water. This “catalytic stage” induced by the Z4A is then followed by a “recombination stage” during which a large decrease of H2 and O2 contents in the gas phase is observed until the total disappearance of the two molecular species. The duration characterizing each stage depends on many factors, among which the initial water loading ratio of Z4A pellets. Recombination was only observed for water loading ratios below around 13% mass. Below this threshold, the lower the loading, the earlier recombination happens. In order to explore this unusual recombination of H2 and O2 (supposed into H2O), a numerical investigation using density functional theory as implemented in the CP2K package was conducted. Ab initio molecular dynamics simulations were performed for various mixtures of those molecules, and for different water loading ratios. In addition, similar simulations were performed for hydrogen peroxide, another possible stable product of water radiolysis. The obtained trajectories were used to compute and compare mean squared displacements and diffusion coefficients to provide insight into the kinetics of the species in a zeolite K4 unit cell, which is a common, smaller substitution lattice for the Z4A unit cell. Water and hydrogen peroxide are rapidly chemisorbed onto the 8R cationic site, while dioxygen and furthermore dihydrogen, remain mobile. These results help in identifying the most probable encounters, in turn suggesting a likely reaction path. In addition, these trajectories provide information on the rate of small timescale events, such as intersite diffusion.
Recently, classical molecular dynamics simulations were started in order to explore the diffusion of the radiolysis products on longer timescales. These trajectories will provide information on the rates of diffusion between cages. The ab initio and classical trajectories thus provide complementary rates for different types of diffusion events inside the zeolite, depending on their timescale. Combined with rates of the main reactions involved in water radiolysis [2], a kinetic Monte Carlo (KMC) program will then be developed to include all events susceptible of playing a role in the recombination process. This program will simulate the full duration of the recombination stage, i. e. a few hundred days for the highest loading rates ratios.

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1207 - ON THE ABILITY OF ALL SILICA ZEOLITES TO ADSORB COMPLEX ORGANIC MOLECULES OF ENVIRONMENTAL CONCERN AN EFFICIENT COMPUTATIONAL SCREENING STRATEGY

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The issue of emerging contaminants like pharmaceuticals and agents of personal care products (PPCPs) becomes increasingly pressing due to the pollution of water resources and the limited ability of conventional wastewater treatment to remove these contaminants.[1] All-silica zeolites have proven themselves to be attractive candidates for the selective removal of organic molecules from aqueous solution.[2] Describing complex chemical systems like these with force field calculations has been employed as a feasible way to investigate large systems.[3] The parameters that a forcefield consist of are often either fitted against experimentally measured properties of a set of model molecules or fitted against the results of ab initio calculations. In most cases the development of the bonded parameters of the forcefield form spectroscopic or ab initio data is fairly straight-forward, while the assignment of parameters describing the intermolecular forces is not an easy task. In the case of ab initio reference data, the atomic charges are typically calculated employing a population analysis which can be strongly dependent on the basis set and the method itself. The deduction of Lennard-Jones parameters to describe the van-der-Waals interaction is similarly problematic, since density functional theory (DFT) methods and even higher-level wave-function based calculations cannot fully describe the dispersion interaction and rely on corrections like the pairwise correction.[4]

In this contribution, combinations of different parameters for organic molecules and silica systems are tested regarding their ability to reproduce DFT reference interaction energies, that have been benchmarked against higher-level wavefunction-based interaction energies. A set of parameters is chosen that is in good agreement with the electronic structure results and yields the least systematic deviations. Having chosen the parameters, they are used to further investigate the interaction of complex organic molecules with all-silica zeolites.

Keeping the limitations of forcefield based calculations in mind they can be a powerful and efficient tool to test a large number of systems in order to decide which ones might be worth considering with electronic structure methods or experimentally. Here we present a hierarchical approach to investigate the ability of hydrophobic zeolites to adsorb PPCPs. Since a pore in a zeolite can only be populated by molecules up to a certain diameter a preselection based on the geometric dimensions of the molecule and the width of the zeolite pore can be done. Forcefield calculations come in here as a tool to sample the conformational space of a given molecule through configurational bias Monte Carlo simulations and to efficiently optimize the crystal structure of the zeolite. In the next step all PPCP – zeolite combinations that would fit from geometric considerations are investigated further by sampling different adsorption sites via simulated annealing to obtain low-energy configurations. On the basis of the trends in interaction energy in combination with other specific properties, a sophisticated choice can be made which PPCP – zeolite combinations should be considered with more accurate methods. Furthermore, suggestions of potentially suitable zeolite absorbents for the removal of certain PPCPs from water resources can be made.

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1264 - STRUCTURE AND OXIDATION PROPERTIES OF THE DISTANT BINUCLEAR VANADIUM V(II) CATIONIC SITES IN SI RICH ZEOLITES

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The distant binuclear cationic sites were firstly identified using theoretical modeling in the context of the study of the N2O decomposition over the Fe(II) cation exchanged ferrierite, the beta zeolite, and ZSM–5 (i.e., Fe– ferrierite, Fe–beta, and Fe–ZSM–5, respectively) [1]. We devised that the presence of the active sites formed by the distant binuclear Fe(II) centers explained the exceptional activity of Fe–ferrierite in comparison with the Fe–beta and Fe–ZSM–5 catalysts [2]. The first chemical step of the N2O decomposition is the formation of the a–oxygen species [2,3] [i.e., (Fe(IV)═O)2+] which exhibits unique oxidation properties reflected in an outstanding activity in the oxidation of methane to methanol at room temperature [3]. Furthermore, we predicted for the first time employing periodic DFT calculations and subsequently confirmed experimentally that the ferrierite zeolite exchanged with other transition metal cations able of the M(II) to M(IV) redox cycle could be employed for the preparation of the a–oxygen species [i.e., (M(IV)═O)2+] using N2O [3].

Moreover, we firstly predicted using the power of periodic DFT calculations that these distant binuclear cationic sites were able to split dioxygen to yield pairs of the distant a–oxygen species. Subsequently, experiments were performed at room temperature and the theoretical prediction of a cleavage of dioxygen to give a pair of the distant a–oxygen atoms was confirmed experimentally and thus splitting dioxygen was discovered [4].

In this contribution, we report on our investigation regarding the structure and oxidation properties of the distant binuclear vanadium V(II) cationic sites as an example of the distant binuclear cationic sites formed by early transition metal cations.

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1303 - MODELLING THE BALANCE BETWEEN CATALYTIC CYCLES IN METHANOL TO OLEFINS CONVERSION OVER H ZSM 5

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Methanol-to-olefins (MTO) conversion over zeolite catalysts, producing mainly olefins from ethylene to C8, is a promising route to bridge the growing 'propylene gap' between supply and demand [1]. However, the complex reaction mechanism at steady-state, i.e. industrially relevant, operation, has hampered further optimization of both the reaction conditions and the catalyst itself. Particularly, the mechanism comprises two catalytic cycles: the 'aromatic hydrocarbon pool' catalysed by aromatics and responsible for short alkenes formation; and the 'alkene homologation' catalysed by acid sites and responsible for long alkenes formation [2]. A kinetic model accurately describing the intertwined functioning of the two catalytic cycles, at steady-state, is still missing from literature.The goal of the present contribution is, hence, to develop a microkinetic model for "steady-state" MTO conversion using experimental data acquired on a highly acidic H-ZSM-5 catalyst, over a large range of conversions (20-80%).

The experiments were performed at temperatures between 375 °C and 450 °C with space times ranging from 0.74 to 15.5 kgcat s molMeOH-1 at 40 kPa MeOH partial pressure. As compared to the previous implementation [3], focusing low conversions, the Single-Event MicroKinetic (SEMK) model developed entails a much more detailed description of the aromatic hydrocarbon pool species. Firstly, the reaction network considers the same elementary reaction steps for the formation of species up to ten carbon atoms, covering all reactions expected. Secondly, a potential impact of the operating conditions on the total concentration of aromatic hydrocarbon pool species is now accounted for, rather than keeping it constant, as an inherent catalyst property (e.g. similar to the acid site concentration).

The model described well the aliphatic product distribution. Also, the ethylene-to-butylene-ratio, a key descriptor of the balance between the alkene homologation and aromatic hydrocarbon pool cycles, was successfully reproduced by the model. Reaction path analyses demonstrated that the model indeed captured the impact of operating conditions on the balance between the two catalytic cycles. At higher temperatures and space time, the alkene homologation cycle gains importance with respect to the aromatic hydrocarbon pool. Within the cycles, cracking reactions are promoted at higher temperatures and intermediate conversions. Furthermore, statistically significant and physicochemically relevant estimates were obtained for the activation energies and adsorption enthalpies.

In summary, the developed model achieved a realistic description of methanol conversion at industrially relevant reaction conditions over H-ZSM-5. The detailed implementation of the aromatic hydrocarbon pool mechanism, for the first time, is deemed particularly relevant for a realistic representation of the delicate balance between both catalytic cycles as a function of operating conditions. Subsequent optimization based on the developed model can lead to the fine-tuning of the operating conditions, and eventually of the catalyst, to maximize propylene formation.

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1307 - AN OPEN SOURCE PIPELINE TO TRANSFORM ZEOLITE SCIENTIFIC PAPERS IN PDF FORMAT INTO MACHINE READABLE FORMAT.

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In the past decades a rapid adoption of digital format to publish new scientific publications has been observed it is expected that the amount of research papers is getting doubled every 5 years.[1] The zeolite field is not an exception, with 21 390 papers on "Zeolite Synthesis" (Web of Knowledge, 24/01/2023). It is impossible for a human analyse all this information manually. Fortunately, text mining techniques, used to retrieve information and data from papers, carried out by a computer can generate a lot of data automatically and ready to be analyzed.[2] However, most of scientific papers are in PDF, being impossible for a computer to analyse it directly since it is very difficult to distinguish the text from the PDF formatting code.[3] There is already open -source software that transforms PDF documents into a machine-readable format, however all of these resources fail to retrieve all the information from a scientific paper. The objective of this work is to transform PDF documents into machine-readable format without losing any information about zeolite synthesis conditions and characterization which could be present in text, tables, and images, since no such type of tool was found in the litterature.

To do so, an open-source automated pipeline was developed to transform PDF files into five different outputs containing whole the article data. Namely, (i) the text body containing not only the text, but also the document structure metadata as HTML/XML format; (ii) the article metadata itself; (iii) the references; (iv) the article tables and legends; and (v) images and legends. The data from ii to v is recorded in a format where not only have the data entries but also information about the data typology. As extracting text from scanned documents is still quite error-prone, the pipeline only transforms text-embedded PDFs (as all current papers are). The structure metadata from the text body can be obtained in different ways that can go from only coordinates and font of each word of the document or information about of the type of entry. By knowing the type of data of each entry of the body text or by using the DOI in the Google Scholar API is possible to obtain the article metadata. An open-source reference manager library retrieves the articles references. A layout parser identifies the tables, images, and legends, after this the same libraries used to get text body file extract the table entries and their coordinates if the table data is embedded in the PDF. If not, an Optical Character Recognizer (OCR) obtains the coordinates, and the text of the table image entries.

Various libraries used to get the text body file of the document have been compared in terms of documents transformation speed and quality of the output. On the other hand, five different layout parser models were compared concerning their speed and table detection accuracy. The pipeline was tested using a dataset of articles about zeolite science, being able to identify with 100% accuracy the document with the text-embedded.

In conclusion, a pipeline to transform PDF scientific papers into machine-readable formats was developed. In the future this pipeline will be used to transform a document corpus containing scientific papers about zeolite synthesis to extract and generate a dataset with zeolite properties and their respective synthesis conditions.

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1147 - TRANSITION METAL MODIFIED MICROPOROUS MATERIALS FOR THERMAL BATTERY

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Due to rapid industrial development and population growth, energy consumption and demand are increasing. As a result, fuel prices are at an all-time high, and economies are facing significant challenges, particularly in the developing countries. The consumption of fossil fuels is causing emissions of greenhouse gases and subsequently having a negative impact on the ozone layer, the environment, and human health. Consequently, governments are making plans and efforts to turn to renewable energy sources. One of these plans is the European Green Deal, which addresses the energy crisis and proposes actions for possible solutions in the EU [1]. Renewable energy sources, such as solar energy, are becoming more popular in the energy supply chain nowadays. However, there is still a barrier between the energy generated from renewable sources and actual energy demands.

According to Eurostat [2], the main use of energy by households in the EU is for heating. With this in mind, researchers are working towards finding appropriate materials for thermal energy storage. Thermal energy storage can be divided into three different categories based on the working principle: sensible, latent and thermochemical. Thermochemical energy storage (TCES) can provide the highest energy storage density of all storages and uses sorption processes and/or chemical reactions of gases on solids or liquids. Materials used for low temperature sorption heat storage include zeolites, aluminophosphates, MOFs, and composites of porous solids and salt hydrates. Furthermore, the commonly used sorbates are water, ammonia, or alcohols, depending on the working material and experimental setup [3].

In this research, we synthesised materials for a thermal battery. The goal was to find materials that are stable under working conditions, easy to produce, and have high adsorption efficiency. Water or ethanol were used as working fluids, depending on the sample. The latter was prepared by catalytic hydrogenation of CO2. Different types of microporous catalytic materials were synthesized: zeolite, aluminophosphate, and MOF, all modified with a transition metal that favours ethanol selectivity (Cu or Co) [4].

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1168 - HIGH COKE DEPOSITION RESISTANCE BY CR6+ LOADING ON ZEOLITE DEFECTS REDUCED REGENERATION IN LOW DENSITY POLYETHYLENE CRACKING

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The increase in plastic waste has induced critical environmental problems, thereby plastic waste should be managed better than ever. Chemical recycling (CR) has recently been considered as an attractive candidate to solve this problem1. In CR, plastic wastes can be converted into valuable products (e.g., monomers or petrochemical feedstocks). Recently, there has been much research on the catalytic cracking of polymers using zeolites. However, the deactivation of zeolites due to coke deposition is a serious problem. Although significant efforts have been devoted toward coking inhibition, the previous methods are not suitable for polymer cracking. Therefore, new approaches are needed to inhibit coke deposition without degrading catalytic performance.

Recently, it has been reported that Cr6+ connected to silanol groups in zeolites is stable and promotes the dehydrogenation of light alkanes2. Since many alkanes are produced in the catalytic cracking of polyolefins, these alkanes are considered dehydrogenated during the reaction. Moreover, aromatics, which are coke precursors, are decomposed via hydrogenation on acid sites of the zeolite. Therefore, hydrogen is generated from the alkanes in the product at the Cr6+ sites, and the hydrogenation and decomposition of the coke precursor at the zeolite acid sites are thought to have inhibited coke deposition. In this study, Beta zeolite was doped with Cr6+, and the effect of the synthesized catalysts on coke inhibition was examined by the catalytic cracking of low-density polyethylene (LDPE). We prepared Cr/Beta(x) samples at a mass ratio of Cr/Beta = x/100 (x = 0.1, 0.5, 1, 5, and 10) by the impregnation method. UV-Vis spectroscopy was conducted to investigate the valency of Cr species in zeolites. The absorption band derived from Cr3+ was only detected for Cr/Beta(5) and Cr/Beta(10), indicating the presence of Cr2O3. Moreover, the peaks derived from Cr6+ were detected for all Cr-loaded samples. We conducted FT-IR spectroscopy to investigate the detailed chemical states of the Cr6+ species. The Cr/Beta samples showed peaks attributed to the Si-O-Cr6+ vibration. Moreover, the weak band assigned to the Cr-O or Cr=O vibration in the Cr6+ species was observed. Thermogravimetric (TG) curves for the catalytic cracking of LDPE under N2 flow at a heating rate of 5 K min-1 were measured to investigate the catalytic performance of Cr/Beta. The decomposition temperature increased slightly when the Cr loading was higher than 5 wt.%, but the Cr loading did not significantly decrease the catalytic activity of Beta zeolite.

In the reaction, Cr6+ species connected to silanol groups performed as a catalyst for the dehydrogenation of light alkanes in the products, and aromatics were decomposed via hydrogenation at the zeolite acid sites. In the ethane dehydrogenation reaction, Cr/Beta generated H2 at a lower temperature than pristine Beta. And it was confirmed that coke precursor was decomposed at zeolite acid sites by using toluene and cyclohexane. Therefore, the synergetic effect of the H2 generation by Cr6+ and the decomposition of coke precursor by zeolite acid sites led to coking inhibition. As a result, it was possible to recycle the obtained catalysts several times without regeneration during the catalytic cracking of LDPE.

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1285 - BIO ETHANOL UPGRADING CATALYSED BY MULTIFUNCTIONAL ZEOLITES

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Global bioethanol production has exceeded 25 billion gallons per year since 2015, predominantly for use as a biofuel. [1] Upgrading of bioethanol into bioacetaldehyde provides a route to many higher value chemicals such as butadiene, pyridine and butanol, with the latter having biofuel applications. [2] Recent work has shown that ZnO supported on Na-MOR zeolite gives rise to very stable ethanol dehydrogenation catalysts (over 120 hours) and increases the catalytic activity per Zn atom, while residual Brønsted acidity promotes ethylene formation. [2] The psuedo 1-dimensional MOR framework has inherent transition state selectivity for linear products over aromatics during ethanol conversion and hence is appropriate for this application. [2] Cu-MFI prepared by Pang et al. shows high selectivity (93%) and productivity (97%) for the non-oxidative dehydrogenation of ethanol to acetaldehyde. [3] Herein, we aim to complement these findings, utilising highly silicious MOR with high Cu loading to explore the conversion of ethanol to higher value chemicals.

Commercial NH4-MOR was hydrothermally dealuminated according to Kolodziejski et al. [4] Subsequent Cu impregnation was performed via ammonia evaporation, as described by Pang et al. [3] Zeolite frameworks were confirmed by pXRD and Si/Al ratios determined by EDXRF. MAS NMR has also been used to understand the Si and Al speciation. Ethanol conversion will be assessed using a HEL FlowCAT flow reactor with online GC-MS-BID and mechanistic pathways will be probed by in-situ DRIFTS analysis. The ammonia evaporation method described by Pang et al. gives rise to high loadings of Cu with high dispersity at the outer surface of the zeolite crystal, avoiding Cu nanoparticle aggregation and stabilising the Cu+ species. [3] Cu+ and Cu0 can therefore play a synergistic role in the non-oxidative dehydrogenation of ethanol. [3]

Looking ahead, we aim to further modify these MOR zeolites with extra-framework metal sites (Mg, Ca, Fe), as well as framework Lewis acid sites (Ti, Sn, Zn) for use in bioethanol upgrading. Studies will be undertaken to determine how the nature and location of the differing catalytic components affects overall catalytic function. Such analysis will expand our structure-activity relationship understanding.

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1358 - ACHIEVING SUPERLONG LIFETIME FOR MORDENITE CATALYSED DME CARBONYLATION

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With the population of ethanol-blended fuel for vehicles, alternative ethanol production technology has been attracting accrescent interests. DME carbonylation is the pivotal technology for ethanol production from resources such as coal, natural gas or biomass, and zeolite mordenite (MOR) is the most promising catalyst for this process[1,2]. The MOR framework is featured with the coexistence of two principal functional channel/cavity, i.e., the unidimensional 12-membered ring (12-MR, 6.5×7.0 Å) channels along the c-axis and the interconnected side pockets with 8-membered ring windows (8-MR, 3.4×4.8 Å). The Bronsted acid sites (BASs) located in the side pockets are the authentic active centers for DME carbonylation, mainly due to the unique space-confinement effect in the side pockets. The 12-MR main channels, nevertheless, are vulnerable to quick coke deposition from DME/methanol to hydrocarbon reaction, resulting in the blockage of channels and quick catalyst deactivation. Indeed, the rapid catalyst deactivation is the primary drawback hindering the application of mordenite-catalysed DME carbonylation.

In order to improve the stability of MOR catalyst, many strategies have been developed, e.g., pyridine modification and selective dealumination by acid/alkali post-treatment. To date, oriented dealumination of the 12-MR channels is challenging, and the stability amolieration is rather limited. And the high toxicity of pyridine makes the pyridine modification strategy less attactive. Novel and alternative strategies to improve the stability of MOR catalyst in DME carbonylation is highly desirable.

Herein, we proposed a new strategy to improve the catalytic performances of MOR-based catalysts for DME carbonylation. The essence of this strategy combines the positive effects of H2 co-feeds in controlling the formation of MTH-derived coke, the enhanced hydrogenation capacity due to Cu presence, and the selectivity adjustment effects of deliberately deposited carbonaceous compounds. Based on the novel strategy, both high activity (0.70 gMeOAc gcat-1 h-1) and MeOAc selectivity (98%), together with long catalyst duration have been achieved. The proposed strategy may provoke new design imagination for zeolite-based catalysts and have potential industrial relevance.

1147 - TRANSITION METAL MODIFIED MICROPOROUS MATERIALS FOR THERMAL BATTERY

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Due to rapid industrial development and population growth, energy consumption and demand are increasing. As a result, fuel prices are at an all-time high, and economies are facing significant challenges, particularly in the developing countries. The consumption of fossil fuels is causing emissions of greenhouse gases and subsequently having a negative impact on the ozone layer, the environment, and human health. Consequently, governments are making plans and efforts to turn to renewable energy sources. One of these plans is the European Green Deal, which addresses the energy crisis and proposes actions for possible solutions in the EU [1]. Renewable energy sources, such as solar energy, are becoming more popular in the energy supply chain nowadays. However, there is still a barrier between the energy generated from renewable sources and actual energy demands.

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In this research, we synthesised materials for a thermal battery. The goal was to find materials that are stable under working conditions, easy to produce, and have high adsorption efficiency. Water or ethanol were used as working fluids, depending on the sample. The latter was prepared by catalytic hydrogenation of CO_2. Different types of microporous catalytic materials were synthesized: zeolite, aluminophosphate, and MOF, all modified with a transition metal that favours ethanol selectivity (Cu or Co) [4].

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CATEGORY: DECARBONIZATION AND CO2 MANAGEMENT

1024 - ORGANIC DYE DOPED ZIF 8 FOR CO2 CAPTURE IN 50% RELATIVE HUMIDITY

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The recent success of CALF-20 has shifted some of the interest of researchers into not only making materials with very high uptakes, but also focusing on high stability and reasonable selectivity for CO2 capture. The proposed setup in use now lends itself to fast adsorption kinetics for which MOFs and ZIFs are well known for. ZIF-8 is the most studied ZIF largely due to its stability and ease of preparation. Its main downside for air remediation application is the lack of functionality in the linkers leading to low selectivity and affinity towards CO2. Functionalisation of ZIF-8 can be done through mixed linker approaches, through embedment of active species into the pores of materials. Mixed linker approaches can be divided into two categories; (a) in-situ, where we add the second linker to the sol-gel or (b) Solvent Assisted Ligand Exchange, where prepared ZIF-8 is soaked in a solution of second linker. On the other hand, metal oxides1, ionic liquids2, organic dyes3 and more have been embedded into ZIFs for increased CO2 uptake. Here we report on the investigation of CO2, water and 50% RH CO2 uptake of ZIF-8 functionalized with organic dye. Dyes investigated were Xylenol Orange (XO), Congo Red (CR), and Bromophenol Blue (BB).

Materials were prepared by in-situ encapsulation . The three organic dyes (OD) were added to the linker precursor solutions of ZIF-8 to produce desired ZIF-8OD composites. ZIF-8 room temperature synthesis in methanol was chosen to avoid difficult removal of less volatile solvents. After synthesis the samples were activated by drying in a vacuum oven at 150°C. The samples were first analysed by using PXRD, SEM and N2 physisorption. Successful encapsulation of OD was indicated by intense colour changes and significant decrease in SBET. Samples after N2 physisorption were then put into a Surface Measurement Systems DVS and their CO2, water and water + CO2 isotherms, to achieve CO2 in 50% RH, were collected at 30°C.

All samples after DVS were then analysed with PXRD to check for sample stability and no change in PXRD patterns was observed. ZIF-8XO and ZIF-8BB showed to have an increase in uptake of dry CO2 compared to pure ZIF-8 while ZIF-8 CR showed a decrease in the uptake. On the other hand, ZIF-8CR had the highest water uptake, compared to ZIF-8BB and ZIF-8XO. While XO does have more functional groups that could lend itself to higher uptakes, it is a much larger molecule than BB and as such decreases the accessible surface area. The humid CO2 isotherms for all three investigated materials showed a decrease in CO2 uptake, compared to dry CO2. In all three cases a 20 – 25 % decrease in uptake was observed. ZIF-XO due to a lower water uptake has a slightly higher humid CO2 uptake than ZIF-8BB with ZIF-8CR again having the lowest uptake .

Organic dyes were shown to be potential pore filling materials of ZIFs to provide additional functionalisation leading to increased uptake and higher selectivity. The ideal dye should be large enough to not easily leave the cages of the ZIF but small enough as not to clog the pores of the material. Ionic dyes like CR increase water uptake which can be potentially utilised for increasing water sorption for water harvesting or for heat storage applications.

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1040 - TANDEM METAL OXIDE ZEOLITE CATALYSTS FOR CO2 UTILIZATION

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Direct catalytic CO2 conversion into key chemicals is a promising field of research for sustainable processes. However, limitations exist for CO2 utilization, i.e., its high activation energy. Tandem catalysts based on mixed metal oxides combined with zeolites (MOx/zeolite) are suitable to combine CO/CO2 hydrogenation on the metal/metal oxide function with the size selective C-C coupling catalyzed by acid sites within the zeolite micropores to produce highly demanded olefins.[1] In this work, we investigate the activation of CO2 on selected MOx/zeolite materials by testing their activity on the CO2 conversion by reverse water gas shift reaction (rWGS, CO2 + H2 → CO + H2O). Oxygen vacancies on mixed-metal oxide surfaces are proposed to be relevant for the activity in both rWGS and CO2 hydrogenation, therefore, we use the rWGS reaction as a proxy to evaluate the potential of the material for the tandem conversion of CO2 into light olefins.

We have studied the activity and structural properties of Cu-Ce-Zr oxides combined with different zeolite frameworks. Among them, SSZ-13 was selected due to its good stability and selectivity to light olefins in the closely related methanol to hydrocarbons conversion. Different synthetic methods were applied with the aim of ensuring a close contact between the two different functions of MOx/zeolite catalysts. Impregnation methods are expected to lead to considerable amounts of Cu2+ migrating into micropores and exchanging the acid sites of the zeolite. For this reason, we also applied a novel synthetic pathway based on the co-precipitation of Cu, Ce, and Zr oxalates in an aqueous suspension of the zeolite powder in NH4+-form (denoted here as oxalate route).

The kinetic parameters of MOx/zeolite and pure MOx materials for rWGS were obtained in the range of 400°C, with different CO2/H2 ratios. Activity tests at high conversions were also performed at typical rWGS temperatures of 600°C. The turnover frequency based on Cu (350°C, H2/CO2=4) is doubled when the oxides are supported on the zeolites. Contributions of the Boudouard reaction, involving removal of solid C deposits, are suggested at 600°C.

Temperature-programmed reduction is used to assess the redox properties of Cu/CuO sites in respect to their interaction with CeZr metal oxides and zeolites. Reduction temperatures of CuO particles are lowered by >25°C for MOx/SSZ-13 materials (~155°C) compared to MOx, which is attributed to a higher dispersion of Cu species.[2] Furthermore, the TPR profile of MOx/SSZ-13 via impregnation shows that a large portion of Cu remains oxidized even at 400°C, which is attributed to ion-exchanged Cu2+ on zeolite acid sites.[3] However, this migration of Cu2+ within the zeolite micropores is hindered in the oxalate route. Following the oxalate route, the precipitation of metal oxides on the external surface of SSZ-13 crystals is achieved, as observed by scanning electron microscopy.

In summary, we have found a successful route to support mixed metal oxides over zeolites for CO2 activation. The obtained materials have a higher activity in rWGS than unsupported metal oxides and therefore show promise as tandem catalysts for the co-conversion of CO2 and syngas to light olefins in a single-step process.

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1041 - UNDERSTANDING THE INTERPLAY OF PORE WIDTH AND AMINE LOADING OF PEI LOADED SILICA ON CO2 ADSORPTION

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A key component to decrease the atmospheric CO2 concentration is the development of carbon capture technologies. Direct Air Capture (DAC) conditions pose particular challenges for gas adsorption due to low partial pressures of CO2 at ambient temperatures. Amine-based sorbents in combination with porous supports and large specific surface area are well-suited for adsorption from low level CO2 sources. Amine-functionalization of porous support materials is commonly achieved via impregnation of amine-containing polymers, e.g., polyethylene imine (PEI).

The goal of this work is to understand the interplay between textural properties and polymer loading of the support on the CO2 uptake in relation to adsorption temperature. In particular, effects like reduced amine accessibility due to pore blocking are investigated and adsorption kinetics are modelled based on obtained adsorption data.

Commercial spherical silica (Chromatorex®) with a pore width between 7 and 50 nm has been wet impregnated with 25, 50 and 75 wt.-% PEI following a modified procedure of Xu et al. [1]. The sorbents were characterized by nitrogen sorption and CHN elemental analysis. For CO2 adsorption experiments, samples were activated at 100 °C in He before being exposed to 450 ppm CO2 in He at 30 – 70 °C. The CO2 concentration in the effluent gas was determined using a NDIR gas detector and uptake was calculated using the formula published by Chatterjee and Schiewer [2].

Generally, larger pores were found to be beneficial at comparable PEI loading, nevertheless, adsorption temperature additionally affects qe. For samples with pore widths ≥ 10 nm, 50 °C yields the highest qe which is proposed to be a result of increased polymer chain mobility and hence increased amine site accessibility at elevated temperatures. At a temperature of 70 °C, a comparable qe of 0.23 – 0.40 mmol g-1 was determined for samples of all pore widths, suggesting that desorption is the main contributor in this temperature regime. For the sample with the largest pore width of 50 nm and 25 wt.-% PEI loading, equilibrium uptake capacity (qe) reached 1.3 mmol g-1 at 30 °C, which is the highest value for similarly PEI-loaded silica ever measured at DAC conditions to the best of the authors' knowledge.

Amine efficiency (fN) as the number of moles of CO2 adsorbed per mole of N is clearly negatively correlated with increasing PEI loadings, as reflected by the decrease in average fN from 0.15 at 25 wt.-% to 0.05 at 75 wt.-%. We assume this is due to decreased amine accessibility as increased polymer loading leads to pore blocking.

In order to better understand key drivers for CO2 adsorption, experimental data is fitted with the kinetic model proposed by Heydari-Gorji and Sayari [3]. Computational simulation of the micro-kinetic model will be applied to calculate kinetic parameters such as adsorption activation energy.

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1129 - HIERARCHICAL ZEOLITE CATALYSTS FOR CYCLOADDITION REACTIONS UNDER CARBON DIOXIDE PRESSURE

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The creation of heterogeneous catalysts for the industrial and fine organic synthesis processes is one of the most valuable research areas in the modern chemical materials science. Zeolites are effective catalysts for a number of acid-base and redox processes. Hierarchical zeolites are materials combining two or more levels of pores. The role of the hierarchy in zeolites is manifested both in an increase the accessibility of zeolite active sites on the surface of inter- or intracrystalline mesopores compared to conventional zeolites and in a change in the strength of acid and basic sites located on the external surface. Such a variation changes the activity and selectivity of catalysts based on hierarchical zeolites. This work presents the results of the catalytic evaluation of hierarchical zeolites in cycloaddition reactions of epoxides under carbon dioxide pressure.

Hierarchical zeolites were obtained by soft template methods using Gemini-type surfactants as structure-directing agents (SDA) [1]. BEA, MFI, MOR and FER zeolites nanosheets, MTW and MOR nanorods and BEA nanoparticles with different chemical composition were obtained [1, 2]. Prepared hierarchical zeolites possess high external surface area and mesopore volume compared to the isostructural bulk zeolites, reaching values Sext and Vtotal up to 330 m2/g and 1.4 cm3/g, respectively, at high accessibility of active sites for bulk molecules (up to 85%). The basic properties of the prepared zeolites were generated by changing the composition of zeolites, ion exchange or fixation basic oxides on the zeolite surface. An important feature of the basic catalysts for this reaction was the neutralization of Brønsted acid sites. Basic properties of zeolite materials by benzene and CDCl3 ad(de)sorption as spectral probes, CO2 volumetric adsorption and TPD of CO2 were studied.

Titanosilicate zeolites with MTW topology and nanorod morphology due to the absence of Brønsted acid sites showed high selectivity towards 4-phenyl-1,3-dioxolan-2-one, however, achieving high conversion of styrene oxide required an increase in the reaction time. Similarly, template-containing hierarchical zeolites demonstrate high catalytic activity and selectivity. The selectivity of such catalysts significantly increases when the exchangeable anion in SDAs is successively replaced in the series Cl– < Br– < I–. When the structure of the initial epoxide is changed, a significant dependence of the catalytic activity of the zeolite catalysts on the electron density on the carbon atom adjacent to the epoxide cycle is noted. In particular, high conversion of epoxides was observed in the case of styrene epoxide, phenoxy- and chloromethyloxiranes, however not for butyl- or cyclohexyloxiranes. The optimal solvent for this reaction was dimethylformamide. When replacing the solvent with dioxane, ethanol, or toluene, the conversion of epoxide decreased due to a decrease in the dipole moment of the solvent molecules and the solubility of carbon dioxide.

Among the studied Cs-forms of hierarchical zeolites, Cs-BEA_np zeolites showed high basic sites concentration and the highest catalytic activity. For a series of Cs-forms of hierarchical aluminosilicate zeolites with different topologies and nanocrystals morphologies, the yield of 4-phenyl-1,3-dioxolan-2-one correlates with the concentration of basic sites (estimated by CO2 adsorption) and the external specific surface area.

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1215 - ETHANE DEHYDROGENATION PROCESS PERFORMANCE EVALUATION OF FE CR AND MO CATALYSTS SUPPORTED OVER ZSM 5

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Ethylene is globally high-demanded building block olefins with increasing demand rate at the manufacturing industry with major polymerization products; Low-density Polyethylene (LDPE), High density Polyethylene (HDPE), Linear low-density Polyethylene (LLDPE). Ethylene is mainly produced from steam cracking process which is considered a high-intensity energy process with conventional reliance on fossil fuel burners as main source of supplied energy. In the production of ethylene, steam cracking operates around 600 oC to 1000 oC depending on in the feedstock used in the process [1]. Consequently, high release of CO2 is associated with the production of ethylene from steam cracking process; a worldwide estimate of 199 million tonnes of CO2 in 2015, projected to increase to 264 million tonnes of CO2 in 2030 (~ a 33% increase) [1]. Therefore, investment into a catalytic process to produce ethylene with reduced energy use through improved efficiency is essential wheather is in a catalytic process or a steam cracking process.

Clearly, the new process must reduce the overall CO2 emissions; it must be less energy-and material-intensive with respect to the onstream processes that aim to replace, it must employ safer and more eco-friendly working conditions and it must be economically viable [2]. Catalytic ethane dehydrogenation is an endothermic process currently operated at temperatures between 550 oC to 800 oC [3]. However, challenges of coke deposition and overoxidation require more experiment validation, rational catalyst design, and process optimization to be completed.

This work studies the catalytic ethane dehydrogenation tests on Fe, Cr and Mo catalysts supported on ZSM-5 with 3 different Si:Al ratios to study conversion and selectivity towards ethylene. The Fe-ZSM-5, Cr-ZSM-5, Mo-ZSM-5 catalysts were prepared with different loadings (5%-10%) wet impregnation over three different ZSM-5 Si:Al ratios 20, 100 and 200. The stated catalysts performance evaluations are conducted using a fixed bed reactor connected to an on-line gas chromatography with FID and TCD detection under the following conditions; 5400 GHSV, mL g-1hr-1, C2H6:N2= 3 and 650 oC to 700 oC. Additionally, XRD, SEM and BET analysis are performed for the fresh and used catalysts to study the ethylene yield in relation to catalysts characterization in terms of crystal size, pore size, volume and specific surface area.

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1291 - DECOMPOSITION OF POLYPROPYLENE IN ORGANIC SOLVENTS USING BETA TYPE ZEOLITE

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Mechanical recycling (MR), chemical recycling (CR), and energy recovery (ER) are the main methods for waste plastics. In order to reduce the amount of waste plastics processed by ER and achieve resource circulation, the CR process is considered to convert waste plastics back into petrochemical raw materials. Waste plastics are dissolved in an organic solvent to remove repellent substances and improve flowability and converted into petrochemical raw materials (C5-C9 products) by pyrolysis and catalytic decomposition. In this study, we used Beta-type zeolite and polypropylene (PP) as the catalyst and the plastic. n-Cetane (n-C16) and 1-methylnaphthalene (1-MN) were used as organic solvents to represent linear alkane and aromatic. The differences in the conversion of PP and product distribution depending on the solvent were studied.

Decomposition tests were carried out using 20 g of organic solvent, 5 g of PP (Mw~370,000), and 1 g of Beta (TOSOH HSZ-900 931HOA Si/Al=15.1). PP, n-C16, or 1-MN and Beta were charged in a 100 mL batch reactor and heated at a rate of 10 K min-1 after N2 gas replacement. The reaction was carried out for 60 min when the temperature in a reactor reached 673 K. After the reaction, the reactor was cooled to room temperature, and the volume of gaseous product was measured. After collecting the gas, the reactor was weighed, and 1.0 g of tetralin was added as an internal standard. A liquid product was collected by pressure filtration. The residue and catalyst in liquid were collected by suction filtration and washed with n-pentane. After drying overnight, the weight of residue was measured, and the conversion of PP was determined. The gaseous product was analyzed with GC-FID for its composition, and then the n-C16 or 1-MN conversion was determined. The distribution of liquid product and the ratio of aliphatic and aromatic hydrocarbons were evaluated using distillation GC and GC-MS.

Reaction tests were conducted using n-C16 or 1-MN and examined differences in the results with and without PP. Without the addition of PP, the conversion of n-C16 was 97.7%, whereas when PP was added, the conversion levels of n-C16 and PP were 96.9% and 97.9%. The addition of PP did not change the conversion of n-C16, and PP was decomposed by nearly 100%. When only 1-MN was reacted with Beta, the conversion of 1-MN was 48.2%, whereas the conversion of 1-MN and PP was 72.6% and 68.2% when PP was added in 1-MN. The conversion of 1-MN was influenced by the addition of PP, and the conversion of PP in 1-MN was lower than in n-C16. The differences in product distribution were also observed depending on the solvent used. When the PP was decomposed using n-C16, C5-C9 aliphatic hydrocarbons were the main product, and aromatic products were few. On the other hand, di-aromatic, generated by the isomerization reaction of 1-MN was the main product in 1-MN. The decomposition products of PP were estimated by subtracting the results with and without PP in using each solvent. A comparison of the decomposition products of PP showed that the ratio of C5-C9 aliphatic in n-C16 solvent was higher than in 1-MN solvent, i.e., about 60% of PP have been converted to C5-C9 aliphatic in n-C16. On the other hand, the alkylation of 1-MN occurred by decomposition products of PP in 1-MN, and then di-aromatic compounds were the main products. Therefore, the fraction of C5-C9 aliphatics was low in 1-MN.

The conversion of PP and product distribution varied depending on the solvent. We considered aliphatic hydrocarbon was suitable solvent to obtain the high conversion of PP and the high selectivity for C5-C9 aliphatic.

1306 - LOW TEMPERATURE SWING ADSORPTION ON ION EXCHANGED ZEOLITES FOR DIRECT AIR CAPTURE OF AMBIENT CARBON DIOXIDE

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Carbon dioxide is the dominant greenhouse gas in our atmosphere and represents the major challenge to our modern society. To achieve the goals of Paris Agreement, aiming at the abatement of global warming and related climate changes, the global average temperature has to be kept well below 2 °C [1]. One necessary building block to reduce the carbon dioxide emissions is its active removal from the atmosphere. According to reports the global carbon dioxide removal is currently around 2 GtCO2/yr. Out of this amount only 2 MtCO2/yr are collected by novel methods such as bioenergy with carbon capture and storage (BECCS) or direct air capture and storage (DACCS).[2] Therefore, the endeavours for the removal of carbon dioxide have to be increased to meet the paris temperature goal and eventually achieve zero CO2 emissions in less than 30 years.[2] This target would necessarily imply the quick development of energy efficent technologies for DAC and its adaption to chemical technologies for the valorization of air-captured CO2 to useful chemicals and fuels. These concepts defines the circular economy aiming at the achievement of zero-carbon emission on the long term.

A crucial part for the successful application of newly developed methods are energy efficiency and process costs. Considering that the basic emitters of CO2 are mainly energy-intensive industry processes it is even more important in the case of carbon dioxide removal to minimize the energy cost for its capture and valorisation. In terms of new developed DAC technologies chemisorption is widely present in the form of surface amines. These amines have an average heat of adsorption in a range from -60 to -100 kJ/mol, depending on the type utilized amines. In contrast the heat for the physisorption on typical adsorbents is much lower; as an example activated carbon has heat of adsorption in the range from -25 to -40 kJ/mole.[3]

Chemisorbing materials have a high adsorption capacity, but with the disadvantage of a relatively higher energy consumption in the thermal desorption step. In contrast, physisorption based adsorbent materials can achieve desorption at much lower energy levels. The main challenge in using these materials, is, however, the need for a low-temperature adsorption step and at the same time often a lower adsorption capacity. Adsorption materials such as zeolites are interesting for such low temperature cycling. These can help to rationalise the cost of the adsorption/desorption cycles. Our approach is to utilise MFI-zeolites modified by ion exchange to study both, the adsorption capacity as well as the sorption cycles, under realistic conditions such as low carbon dioxide concentrations, presence of water and atmospheric temperatures and pressures.

1320 - UNDERSTANDING CO2 SORPTION MECHANISMS IN SUSTAINABLE CELLULOSE AND CHITOSAN AEROGELS

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Carbon dioxide (CO2) is the most greenhouse gas emitted by human activities and one of the biggest responsible for climate changes. Thus, CO2 emissions must be dramatically reduced to mitigate global warming. Several technologies have been proposed to remove CO2 from the air or flue gases, but amine-scrubbing is currently the most used method to remove CO2 at industrial-scale applications. Amine-based liquid absorbents suffer from several limitations such as poor chemical stability, environmentally unfriendly, and demand high-energy regeneration stages [1]. Alternatively, the adsorption technology uses solid adsorbents, which are promising candidates for large-scale carbon capture due to their lower regeneration energy requirements and durability over many cycles, two of the main cost drivers in CO2 capture technologies [2].

The practical implementation of large-scale carbon capture technologies requires the availability of CO2 selective and low-cost materials that are renewable . Polysaccharide-based adsorbents are abundant, renewable and biodegradable [3], making them a promising candidate for this use. However, the CO2 capture mechanisms in these materials remain largely unknown. In this work, CO2 sorption mechanisms on cellulose and chitosan aerogels were studied by solid-state NMR spectroscopy and DFT calculations. A combination of 1D 13C cross-polarization (CP), 2D 13C-{1H} LG-CP HETCOR and CP kinetics NMR experiments were performed to characterize confined chemisorbed and physisorbed CO2 adsorbed species. First-principle DFT calculations were used to aid the NMR assignments of the different types of adsorbed CO2 species. We show, for the first time, that while cellulose aerogels adsorb CO2 purely via physisorption processes, chitosan aerogels instead capture CO2 via chemisorption and physisorption processes. The chemisorbed species in chitosan aerogels were assigned as ammonium carbamate and carbamic acid species. These results contribute towards a better understanding of the adsorption processes in these materials, and it is a steppingstone for future improvements in the performance of these sustainable solid sorbents.

1336 - CATALYTIC CO2 HYDROGENATION TO FORMIC ACID BY AN INDIRECT HYDROGEN SOURCE

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Carbon dioxide emissions are increasing day by day, being a major contributor to global warming and the earth's temperature rise. The scientific community is searching for different routes in order to mitigate greenhouse gases. CO2 is an abundant, cheap, recyclable, and nontoxic C1 source and can be converted into several important fuels and commodity chemicals [1,2]. In many CO2 utilization reactions, CO2 hydrogenation to methane, methanol, formic acid, and acetic acid has acquired a high impact due to the vital advantages of the end products [3]. Formic acid production via CO2 hydrogenation has been attractive due to its wide range of use in many industrial applications such as agricultural, leather, and dye industries. CO2 hydrogenation via an indirect hydrogen source has been studied by several other routes such as electrochemical reduction, photocatalytic reduction, and hydrothermal reduction. Hydrothermal CO2 reduction to formic acid by using an indirect hydrogen source was studied with metals, metal/metal oxides, and multi-metallic catalysts. Most of the previous reports used NaHCO3 as a CO2 source as the direct use of CO2 is less practiced. Hydrogen storage materials are playing a vital role in the hydrogen economy society. Hydrazine is one of such hydrogen storage material but explosive in nature. So, the monohydrated hydrazine (H2NNH2·H2O) has a large hydrogen capacity of 7.9 wt.%, it is less explosive and safe to use. In the present study, novel ZrO2-based catalysts by two methods namely, physical mixing and co-precipitation methods were synthesized and evaluated for CO2 conversion to formic acid.

ZrO2 support was synthesized by the precipitation method with ammonia as a precipitating agent. The obtained white precipitate was washed, dried, well-ground, and calcined at 300°C for 4 h. 6 wt.% Mn metal was used to synthesize the catalysts by physical mixing (Mn+ZrO2) and co-precipitation methods (Mn-ZrO2). All the prepared catalysts were reduced at 350 °C for 2 h in 5% H2 balanced Ar flow.

The catalysts exhibited high specific surface areas of 175, 158, and 191 m2/g for ZrO2, Mn+ZrO2, and Mn-ZrO2, respectively. All the catalysts have cylindrical-like pore channels with microporous nature that attributed to the high surface areas to the catalysts. In the physical mixing method, high pore blockage is observed which reduces the catalyst surface area. XRD study shows two broad peaks indicating that the catalysts are in an amorphous phase. Sharp and intense peaks are observed in Mn-added catalysts, these peaks are Mn metallic peaks that were observed in the physical mixing method catalyst. Whereas in the co-precipitation method catalyst showed no peaks related to the Mn metal. The XPS study also confirms that the majority of Mn is in its lower oxidation/metal nature in the Mn+ZrO2 catalyst. The surface coverage of metallic Mn on the support leads to an increase in the Mn2+/Mn3+ ratio in the Mn+ZrO2 catalyst. In CO2 hydrogenation via an indirect hydrogen source, the first step involves the hydrazine decomposition to hydrogen. The effective hydrazine decomposition is carried out on the metal surface. So, the catalyst synthesized by the physical mixing method having a rich metallic surface (Mn2+/Mn3+ ratio) leads to improving the catalytic conversion of CO2 to formic and acetic acid. Therefore, Mn+ZrO2 is showing an enhanced catalytic activity compared to Mn-ZrO2.

1011 - RESEARCH INTEGRITY ETHICS IN RESEARCH

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This presentation deals with general descriptions of ethics in research, ethical problems in the daily life of researchers as well as addressing offences related to ethics in research. Research ethics govern the standards of conduct for scientific researchers, and it is important to adhere to ethical principles in order to protect the dignity, rights and welfare of research participants. Moral and ethics are important aspects to be taken into account with respect to scientific research.
Expectations from the scientific community related to research will be addressed as well as a responsible conduct of research. National and international actions to enhance ethics in research will be presented and discussed and the responsibility related to internal and external cooperation partners will be outlined. As an example, the Singapore Statement on Research Integrity (World Conferences on Research Integrity) defines the meaning of Research Integrity by establishing systems that favour the quality, relevance, and reliability of research [1]:
Honesty in all aspects of research.
Accountability in the conduct of research.
Professional courtesy and fairness in working with partners.
Taking care of research on behalf of others.

Furthermore, forms of scientific ethical misconduct will be addressed [1]:

Fake results (falsifying or fabricating data).
(Self-) plagiarism: present others' (own) data/text as new.
Image manipulation: "photoshopping".
Dual submission: to different journals at the same time.
Fractured publication: "salami slicing".
Authorship misrepresentation: non-contributing co-authors, missing co-authors.
Fake peer review and citations rings.
Paper mills: producing manuscripts at scale (from research data, to ghost-written fraudulent, or fabricated manuscripts).

All of the above can have serious consequences.

The researcher's daily business will be highlighted including common understanding and reporting of critical items. Responsible research and innovation will be underlined through the policy and charter for researchers announced by the European Union. By the way, the European Union requests recently to establish an "Ethical Advisory Board" besides the Steering Committee by performing larger European Union projects.

Finally, independence, hability, collaboration, scientific authorship and contract research aspects will be highlighted, as well as commercialization of R&D results [2].

We all have a role to play in Research Integrity! Everyone involved in research has a role to play in research integrity, no one can do this alone! Upholding the values of integrity is a shared responsibility [1].

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1138 - SOLVOTHERMAL SYNTHESIS OF COVALENT TRIAZINE FRAMEWORKS AS METAL FREE HETEROGENEOUS PHOTOCATALYSTS IN COUPLING OF BENZYLAMINE

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Covalent triazine frameworks (CTFs) are a new type of porous organic polymers (POPs) which have some unique properties through their aromatics C=N linkage (triazine building unit) and the absence of weak bonds, mainly used as photocatalysts due to their chemical and thermal robustness, their highly conjugated and nitrogen rich nature, facile syntheses, and most important unprecedented structural variability. In particular, CTFs are well known for various applications, such as separation and storage of gases, energy storage, heterogeneous catalysis and photocatalysis.

Most of the reported CTFs are amorphous or semicrystalline due to their ultra-strong bonds, because in the highly dynamic condensation reactions, its stronger bonds show more difficulty to form ordered structures. CTFs were often classified as conjugated microporous polymers (CMPs), which are a class of amorphous porous polymers that combine π-conjugated skeletons with permanent nanopores, in contrast to other porous materials that are not π-conjugated and conventional conjugated polymers that are nonporous. Currently, it is important to focus further research lines on new efficient synthetic strategies for metal-free and non-toxic heterogeneous photocatalysts, and additional insights into the photocatalytic processes in organic transformations are still necessary. In this work, we present a solvothermal method to obtain a new class of crystalline and semicrystalline Porous Organic Materials based on Covalent Organic Frameworks (COFs) with various photoactive building blocks structurally incorporated. Through the discovery of these new methods, it was possible to find CTFs with ultra-strong bonds that can actually form an ordered structure under certain conditions.

These materials were employed as metal-free heterogeneous photocatalysts in the coupling of benzylamine, since imines are interesting high value products used as building blocks in organic chemistry. Incorporation of photoactive triazine building blocks in COFs can endow the material with photocatalytic activity under UV and Visible light at room temperature, allowing the selective aerobic oxidative coupling of benzylamine to N-benzylidenebenzylamine. The lack of conversion obtained in the dark or in the absence of catalyst demonstrate the true photocatalyic properties of the photoactive CTFs prepared herein.

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1166 - HYDROGEN PRODUCTION BY WATER ELECTROLYSIS CELL USING ZEOLITE MEMBRANE

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Hydrogen (H2) has a prominent potential as a source material for power generation by fuel cells and carbon recycling technologies via industrial catalytic reaction to realize a carbon neutral society. Hydrogen can be produced by water electrolysis, and the water electrolysis using a proton-conducting solid electrolyte can produce H2 with high efficiency, which has already been practically used. However, the proton-conductive solid electrolytes membrane used currently are strongly acidic polymer membranes consisting of fluorinated-sulfonic acid, hence rare and expensive precious metals must be used for the electrodes. Therefore, alternative proton-conductive solid electrolyte acting at neutral conditions are strongly required to use a base metal that is cheaper than a precious metal as the electrodes, which can reduce the hydrogen production cost. We previously reported that H-beta-type zeolite can promote proton conduction in pure water.[1] In this study, we constructed a electrolytic cell composed of a zeolite membrane coated by spraying its powders onto the electrodes to produce H2 by water electrolysis from pure water. We investigated the effects of the amount of silanol nest, particle size and crystallinity of zeolite on the water electrolysis efficiency. In addition, hydrogen production efficiency was investigated.

The zeolite used in this study was H-beta-type zeolite with 92.5 of Si/Al molar ratio. Pulverization was performed using a planetary ball mill at a rotation speed of 600 rpm for 10 hours. The powder obtained after the treatment and the untreated zeolite were defined H-BEA-92.5_M and H-BEA-92.5_S, respectively. A water electrolysis cell was constructed as follows. First, a circular carbon electrode with a gas diffusion layer was placed on a hot plate at 70°C, and then catalyst ink (anode: IrOx, cathode: Pt/C) was applied onto the electrode by spraying. A hot plate was heated to 90°C, and H-BEA-92.5_S or H-BEA-92.5_M dispersed in pure water was sprayed onto the catalyst. After evaporating the water, the zeolite-coated surfaces were put together, and a gold mesh serving as a current collector was brought into close contact with the gas diffusion layer side to form a water electrolysis cell. The water electrolysis cell was immersed in pure water at 80°C, the current collector was connected to a potentiogalvanostat. The water electrolysis was conducted by constant voltage application measurement at a potential of 0.2 to 2.0 V.

According to the current–voltage curves obtained on water electrolysis by the cell consisting of the zeolite before and after pulverization, the current density did not increase till the theoretical electrolysis voltage (1.18 V at 80°C) in either curve, indicating that electron conduction was negligible. At 1.4 V for H-BEA-92.5_S and at 1.6 V for H-BEA-92.5_M, the current density significantly increased and the generation of gases from both anode and cathode was observed when the water was split. Also, with an increase in the voltage, the difference in the current density between H-BEA-92.5_S and H-BEA-92.5_M became larger. These results suggest that the zeolite membrane functions as a proton-conducting solid electrolyte. Furthermore, H-BEA-92.5_M was applied onto the electrodes more smoothly and densely compared to H-BEA-92.5_S. These results indicate that the maintenance of the crystallinity of zeolite is more dominant than the coating condition of the zeolite on the hydrogen generation by a water electrolysis cell using a zeolite membrane as a proton-conducting solid electrolyte. In summary, we succeeded in the generation of hydrogen by a water electrolysis cell using a zeolite membrane as an electrolyte.

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1275 - ONE POT METHOD OF PRODUCTION CARBOXYLIC ACIDS FROM CELLULOSE DERIVED GLUCOSE OVER NA BEA ZEOLITE.

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Lignocellulosic biomass shows great potential for the production of liquid biofuels, given its large-scale availability, low cost, and low greenhouse gas emissions. It is also the starting material for obtaining many valuable chemical feedstocks, especially acids such as levulinic acid, oxalic acid, lactic acid, and formic acid [1-5]. The idea behind the production of chemical raw materials based on waste lignocellulosic biomass is to turn industrially useless waste into useful raw materials. The purpose of the process is to develop a method for obtaining green C1–C5 carboxylic acids from cellulose-derived glucose.

In our work, zeolite catalyst based on sodium version of synthetic BEA (Clariant) with physicochemical properties presented in Table 1 was used, without carrying out any modifications. The samples were dried at 100 °C for 5 h and calcinated for 5 h at 450 °C. Glucose conversion in heterogeneous conditions was carried out in the temperature range of 200–250 °C for 1–5 h using Na-BEA (0.1 g and 0.6 g) in Teflon-filled autoclaves. The analysis of the obtained products during glucose conversion was performed using the HPLC-RID system.

When the process is carried out at 220 °C for 2 h, products such as levulinic acid and lactic acid are produced. The conversion of glucose at 250 °C for 1 h, regardless of the amount of Na-BEA used as a catalyst, gives three products: levulinic acid, lactic acid and formic acid. From the collected data, it can be seen that conducting heterogeneous catalysis with a smaller amount of Na-BEA under mild conditions gives lactic acid with an efficiency of 100%. Our results show that Na-BEA catalyst at a relatively lower temperature of 200 °C, low zeolite content (0.1 g) and 5 h of process, the process is 100% efficient at succeeding in the very selective production of levulinic acid. Such a result is interesting from a practical point of view due to lower energy consumption.

1299 - LOW TEMPERATURE HYDROGENATION OF CARBON DIOXIDE TO METHANOL BY CATALYSTS BASED ON MONO BI TRINUCLEARS DERIVATIVES OF FERROCENE AND BENTONITE DERIVED MESOPOROUS SUPPORT

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Hydrogenation of carbon dioxide to methanol is one of the most efficient ways of CO2 utilization [1, 2]. Due to the low equilibrium conversion of CO2 to methanol at a high temperature, it is extremely important to develop efficient processes for the catalytic hydrogenation of CO2 operating at a low reaction temperature [3]. The presented report presents the results of the development of a technology for obtaining a mesoporous material based on bentonite and one-, two- and three-nuclear derivatives of ferrocene - C5H5FeC5H4-C(CH3)2OH (I), [C5H5FeC5H4]2C(CH3)OH (II), [C5H5FeC5H4]3C-OH (III) and their studies as catalysts for the reaction of low-temperature hydrogenation of carbon dioxide into methanol. Studies show that ferrocene derivatives I-III deposited on BDMM (bentonite-derived mesoporous materials) with an iron content of 0.5-1 wt.% promote the hydrogenation of CO2 with a selectivity for methanol equal to 80-85% at a reaction temperature of 1450C, a pressure for CO2 and H2 - 0.8 and 4.2 MPa, respectively. BDMM was obtained by treating bentonite first with alkali (NaOH) followed by repeated washing with bidistilled water and then with acid (HCl). Further, the obtained samples were again washed, dried, calcined in an air stream at 4000C for 4 hours and reduced at the same temperature in a hydrogen stream for half an hour. The bentonite of the Dash-Salakhli deposit of the Republic of Azerbaijan was used as bentonite. Ferrocene derivatives I-III were impregnated to BDMM from organic solutions. The elemental and phase composition of the catalysts before and after treatment, application of active components, calcination and reduction was determined using an XRF S8 Tiger X-ray fluorescence spectrometer and an XRD D2 PHASE, Bruker X-ray diffractometer. with Energy Dispersive Elemental Analyzer Hitachi S-3400N/EDS. The textural parameters (specific surface area, volume, and pore size) were determined from N2 adsorption-desorption curves. The infrared and electron magnetic resonance spectra of the samples were recorded, respectively, using an FTIR Alfa Fourier spectrophotometer, Bruker in KBr pellets, and an EMXmicro radiospectrometer, Bruker, Germany. The dependence of the activity and selectivity of catalysts with respect to the target reaction product, the distribution of iron in the catalyst structure, the phase composition of catalysts, IR and EMR spectra on the composition of ferrocene derivatives and the temperature of preliminary reduction of catalysts with hydrogen has been established. The structure-activity relationship for this catalytic system has been studied. It is assumed that subnanometer-sized iron particles formed during the reduction of iron compounds I-III are catalytically active centers of the methanol formation reaction.

1328 - EFFECT OF PRECURSOR ON THE ACTIVITY OF MNOX NA2WO4 MORDENITE CATALYST FOR DIRECT CONVERSION OF METHANE TO C2 HYDROCARBONS

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Over the past 10-15 years, a fairly large number of works have been published on the preparation of MnNaW/SiO2 catalysts, the study of their structural and catalytic features in the oxidative conversion of methane (OCM). Oxide systems with such composition are considered promising catalysts for this reaction [1–3]. The organic structurants, complexing reagents used in the preparation of these catalysts, their effect on their activity and structural characteristics deserve close attention.

In this report the effect of precursors (citric acid, urea, triethanolamine) on the activity of MnNaW/Mordenite catalyst for the oxidative condensation of methane (OCM), its morphology, distribution of active elements in the structure of catalyst, phase composition, textural, magnetic, and catalytic properties were studied in order to optimize the preparation technic of this catalyst.

The synthetic mordenite with molar ratio equal to 20, manganese acetate tetrahydrate Mn(CH3COO)2*4H2O, sodium tungstate dihydrate Na2WO4*2H2O, citric acid, urea and triethanolamine as precursors were used for preparation of catalysts. The prepared samples were calcined at 850 °C for 2, 4 and 10 hours, then characterized by scanning electron microscopy with energy dispersive elemental analysis (SEM/EDS), X-ray diffractometry (XRD), electron paramagnetic resonance (EPR), thermoprogrammed oxidation (TPO), N2 adsorption-desorption measurements and tested as a catalyst for the OCM reaction. Studies have shown that catalysts of the composition 2Mn-0.8Na-3.2W/SiO2, obtained using triethanolamine as a modifying reagent, had a higher activity than catalysts obtained using urea and citric acid. Studies also show that powder morphology, particle size, and their surface area are directly related to the composition and amount of gases released during the preparation of catalysts. The emitted gases disperse accumulations of particles, creating pores between them. The conversion of methane with the participation of this catalyst reached 45%, and the yield of C2 hydrocarbons was 29% at atmospheric pressure, a reaction temperature of 800°C, and a molar ratio of 4. Methane activation along with the formation of C2 hydrocarbons increased markedly at higher temperature, but was deactivated due to carbon deposition, as confirmed by the TPO data.

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1338 - CLEANER ONE POT TRANSFORMATION OF GLYCEROL TO GREEN LIQUID FUEL USING CU BASED OXIDE DERIVED FROM HYDROTALCITE STRUCTURED MATERIALS

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Glycerol was produced in excess in recent years due to increasing biodiesel production. It is used for various applications due to its versatile chemical properties and cost-effectiveness. It could be used as a renewable raw material for the food industry, fuel additive, pharmaceutical products and others. In recent years, research on glycerol has mainly focused on adding value to glycerol in catalytic processes [1,2].

In this study, the catalytic activity of Cu-based oxide catalysts in the hydrogenolysis of glycerol was investigated, and the effect on the selectivity of 1,2-propanediol (1,2-PDO) with the different Cu/Al molar ratios was observed. The glycerol conversion/1,2-PDO selectivity was found to be dependent on the metallic sites and surface acidity of the Cu-based catalyst. The surface acidity and metallic sites of Cu nanoparticles were significantly improved with the increase of Cu/Al mole fraction in the catalyst. The efficiency of the Cu-based oxide catalyst was attributed to the well-dispersed Cu and the presence of acidic sites. As expected, the 3CuAl catalyst is an excellent catalyst for the high selectivity of 1,2-PDO (84.2%) and the conversion of glycerol (83.5%) achieved under optimal reaction conditions. The selectivity of 1,2-PDO was closely related to the acidic sites and the metallic sites of the catalyst, which effectively enhanced the effect of C-O bond cleavage of glycerol. Alumina-mediated copper (especially 3CuAl catalyst) contained more acidic active sites on the surface, and these sites interacted well with intermediate acetol species. This interaction resulted in increased 1,2-PDO selectivity. The synergistic effect of alumina and Cu on the 3CuAl catalyst is an important contribution to the effective control of 1,2-PDO formation. Moreover, the ANN model was developed and validated with experimental results for glycerol conversion and 1,2-PDO yield in the hydrogenation reaction. The results presented are promising and useful for determining the key relationships between the reaction conditions and the targeted performance. This can help in the development of efficient design or screening of heterogeneous catalysts with targeted properties.

1368 - SYNTHESIS AND LUMINESCENCE STUDY OF ZR MOF 808 BEFORE AND AFTER RHODAMINE B DYE SOAKING

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Metal organic frameworks (MOFs) are materials well known for their high surface and catalytic properties as well as because they are relatively easy to synthesize and, in some cases, extremely flexible.[1] Recently, there has been also a growing interest in the optical properties of these materials, particularly in luminescence, which has potential applications in various fields, such as sensors, LEDs, scintillators, and bioimaging agents. One very promising route to obtain luminescent MOFs is to load them with organic luminescent dyes. This approach is both highly versatile and straightforward, as a vast array of dyes with diverse optical properties are readily available. As a result, it is feasible to cover the entire visible spectrum and even the near-infrared region in terms of emission. So, it is possible to tailor the optical properties of a material by properly combining MOFs and dyes.[2] Nevertheless, for this approach to be viable, it is essential to utilize MOFs that can withstand post-synthetic loading and possess adequately sized cages to effectively accommodate the typically large dye molecules. From this perspective zirconium MOF-808 is a valid candidate for loading organic dyes because it is well known to be chemical and thermally stable. In addition, it possesses high surface area (~2000 m2/g) and cages with diameter of 18 Å, that is comparable to the size of many organic dyes.[3]

Here we present a pioneering study on the luminescent properties of bare zirconium-based MOF-808 and on the same MOF loaded with Rhodamine B luminescent dye (MOF-808@RhB). In this work MOF-808 was synthesized by room temperature approach and later loaded with Rhodamine B by a post-synthetic soaking. The structural and morphological characterizations were performed by XRD, FTIR-ATR, TGA, SEM, and by estimation of the specific surface with the BET method, while luminescence properties were studied by time resolved photoluminescence (TRPL), both for dry powders and for powders dissolved in distilled water. Our results show that upon laser excitation at a wavelength of 280 nm, bare MOF-808 exhibits a wide luminescent band peaked at 425 nm which decays in the nanosecond temporal range. Regarding MOF-808@RhB, we were able to observe both the luminescence bands of the bare MOF-808 and of the embedded Rhodamine B, with the latter red-shifted compared to free Rhodamine in water. Surprisingly, we have found that the two bands observed for MOF-808@RhB share the same decay lifetime which, interestingly, is different from the one pertaining to MOF-808 and Rhodamine B taken alone.

The reported study has permitted us to obtain for the first time a comprehensive description of the luminescence properties of bare MOF-808 and of MOF-808@RhB interaction. Furthermore, our data points out that the luminescence properties of Rhodamine B are significantly modified by the interaction between the luminescent molecule and the hosting matrix. These results have strong impact on fundamental research focused on luminescent MOFs, shedding new lights on the effects of the host-guest interaction, and making possible prediction for analogue systems.

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1248 - UTILIZATION OF WASTE GRANITE POWDER IN POROUS CEMENT-BASED MATERIALS FOR SUSTAINABLE CONSTRUCTION

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Production and consumption of cement-based materials provides global foundation to society and the worlds economy [1]. Cement-based materials are usually very porous and heterogonous. The challenge is also to reduce carbon footprint of cement-based materials [2]. On the other side the challenge is to reduce the amount of pores in the structure of cement-based materials. Both goals can be achieved thanks to industrial wastes that can be sourced from aggregate quarries. Its utilization is must be done in the context of sustainable future construction technology [3]. One of the recent examples is waste granite powder sourced from granite quarries [4]. The size and nature of the waste granite powders give us a hope that thanks to the filling effect the pores in cement-based materials can be successfully filled. Also, the chemical composition as well as particle size characteristics make this by-product of mining industry an attractive additive to be used in durable and sustainable cement-based matrices [5]. There are no studies in literature concerning the assessment of the effect of waste granite powder modifying porous cement-based materials on its porosity. Considering the above the main goal of this presentation is to show the possibility to incorporate waste granite powder sourced from industrial wastes as functional additive into sustainable and environmental-friendly cement-based materials. The goal is also to present results concerning the porosity analysis of cement-based materials modified with waste granite powder. The porosity analysis has will be performed using two different techniques conventional water immersion as well advanced analysis of images obtained from scanning electron microscopy (SEM). The results will be compared each other as well as the detailed discussion will be provided.

Acknowledgments

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CATEGORY: OPERANDO INVESTIGATIONS

1016 - EFFECTS OF HYDROTHERMAL AGEING ON THE DYNAMIC NATURE OF ACTIVE SITES IN CU EXCHANGED SMALL PORE ZEOLITES

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Cu-exchanged small-pore zeolites with CHA and AEI framework are currently the catalysts of choice for selective catalytic reduction of nitrogen oxides with ammonia (NH₃-SCR) owing to better hydrothermal stability (compared to medium-pore zeolites) and high catalytic activity across a wide range of temperatures. During NH₃-SCR, Cu acts as a redox shuttle and exists in both Cu¹⁺ and Cu²⁺ oxidation states coordinated either to the reactants (NH₃, NOx) or to the O-atoms present in the zeolite framework. The oxidation state and coordination environment of the active Cu species varies dynamically depending on the reaction conditions (reaction temperature, concentration of the reactants, etc.).

During typical use, these catalysts are exposed to elevated temperatures in the presence of water resulting in a significant decrease in their catalytic activity over time. The decrease in the catalytic performance upon hydrothermal ageing is typically attributed to the changes in the coordination structure of active Cu species. However, the exact nature of this effect is still not fully understood. Utilizing <i>operando</i> X-ray absorption spectroscopy (XAS) supported with kinetic measurements and theoretical simulations, we present a comprehensive study elucidating the effects of hydrothermal ageing on the electronic and coordination structure of active sites in Cu-SSZ-13 and Cu-SSZ-39 zeolites during NH₃-SCR.

<i>Operando</i> Cu K-edge XANES and EXAFS were measured on fresh and hydrothermally-aged Cu-exchanged zeolites under NH₃-SCR conditions between 373 K and 823 K. Using principal component analysis, MCR-ALS analysis, and linear combination fitting, the distribution of Cu-species in the zeolites was expressed as a combination of four different principal components: (i) mobile Cu¹⁺ coordinated to ammonia, (ii) mobile Cu²⁺ coordinated to ammonia, (iii) Cu¹⁺ coordinated to the zeolite framework, and (iv) new Cu²⁺ species formed upon hydrothermal ageing. The fourth component was only observed in the hydrothermally aged zeolite samples. The identity of these components was further verified both experimentally by exposing the catalyst to different gaseous mixtures and measuring in situ X-ray absorption spectra and computationally by density functional theory calculations.

The Cu²⁺ species formed upon hydrothermal ageing were shown to be primarily active for NH₃-oxidation, but not for NH₃-SCR, resulting in the observed decrease in the catalytic performance of the hydrothermally ages zeolites, especially at high temperatures. Hydrothermal ageing also resulted in the formation of extra-framework Al (EFAl) as evidenced by Al K-edge XAS and ²⁷Al NMR. Formation of EFAl resulted in a partial collapse of the zeolite structure thereby imposing further mass transfer limitations within the zeolite pores. The Cu-ion and zeolite structure stability varied as a function of zeolite framework; with AEI framework showing better hydrothermal stability compared to CHA. The Cu-ion and zeolite structure stability also varied systematically with Cu loading as well as with Si/Al.

1075 - MULTISPECTROSCOPIC STUDY OF MOLECULAR OXYGEN DISSOCIATION OVER ZEOLITES

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Molecular oxygen is easily available, cheap and eco-friendly thus it can be considering as a very promising oxidant. However, for the oxidation of hydrocarbons by O2 its activation over heterogeneous catalysts is needed. Recently, it was found that iron ferrierite (Fe-FER) exhibited extraordinary properties toward O2 dissociation over binuclear cationic centres [1,2]. It was shown that the cooperation of divalent bare Fe located in β cationic positions of FER facilitates O2 splitting and formed an active oxygen form [Fe(IV)=O2-]2+ called α-oxygen. This [Fe(IV)=O2-]2+ species can easily oxidize methane to methanol at ambient conditions, which subsequently releases the Fe-FER surface without using effluent.

This study presents a FTIR and Mössbauer spectroscopy investigation of the formation and evolution of [Fe(IV)=O2-]2+ originating from molecular oxygen splitting over Fe-FER and methane oxidation at 220 °C. In this research, a commercially available FER zeolite (Si/Al 8.6, Tosoh Corp.) was selected due to the high concentration of Al pairs (66%) responsible for predominant stabilization of iron as Fe(II) in cationic positions. The FER was ion-exchanged with NH4NO3 to NH4-form. Subsequently, NH4-FER was impregnated by FeCl3 dissolved in acetylacetone with iron concentration guaranteeing in the final product the molar ratio Fe/Al 0.1. As was previously confirmed this iron loading in FER results in exclusive stabilization of iron as bare cations with predominant fraction of Fe (II) in β cationic position forming binuclear centres, which are curtail for O2 splitting.

The FTIR and Mössbauer study reveal that Fe-FER sample evacuated at 450 °C contained exclusively Fe(II) cations, which are predominantly (80 %) located in β cationic position. In-situ Mössbauer study demonstrated that O2 treatment of Fe-FER at 220 °C led to oxidation of Fe(II) to [Fe(IV)=O2-]2+. The interaction of oxidized Fe-FER with CH4 resulted in reduction of [Fe(IV)=O2-]2+, and obtain iron species with Mössbauer parameters similar to those detected in evacuated samples. In-situ FTIR spectroscopy results confirmed that the intensity of the band at 907 cm-1 typical for Fe(II) in β cationic (most pronounced band in the spectrum of evacuated Fe-FER) decreases with increasing intensity of the band characteristic for the [Fe(IV)=O2-]2+ (897 cm-1). Interaction of the [Fe(IV)=O2-]2+with CH4 at 220 °C results in the instantaneous vanishing of the band at 897 cm-1 and re-formation band typical for Fe(II) sitting in β position in FER. Both in-situ Mössbauer and FTIR study results confirm for the first time the splitting of O2 at 220 °C over binuclear Fe(II) structure in FER.

FTIR analysis of gaseous products of [Fe(IV)=O2-]2+ and CH4 interaction at 220 °C confirm the presence of the bands at 2926, 2827 cm-1, characteristic for the vibrations of methoxy species, indicates the methanol formation. These results clearly indicate that [Fe(IV)=O2-]2+ complex can be identified as species responsible for direct methane to methanol oxidation. The stability of [Fe(IV)=O2-]2+ at elevated temperatures extends the utility of the Fe-FER system for methane oxidation in a wide temperature range, which may facilitate the oxidation products desorption and thus make the process more attractive for industrial purposes.

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1115 - ULTRASONIC DIAGNOSTIC FOR INVESTIGATING THE SEED FORMATION OF LINDE TYPE Y IN ABSENCE AND PRESENCE OF MORPHOLOGY MODIFYING AGENTS

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Nowadays, in-situ monitoring of structure formation processes are attracting increasing attention, since it allows to obtain information, which might be missed by ex-situ characterization alone. In-situ ultrasonic diagnostic is a valuable technique, since it is (i) non-destructive, (ii) robust and (iii) offers sufficient time resolution [1]. In addition, the ultrasonic transducers can be placed even outside of the reaction vessel, thus, not affecting the reaction mixture itself. Using the pulse-echo method, a high frequency pulse is sent through the reaction gel, reflected at the wall of the reaction vessel and the transducer can measure the intensities of the multiple echoes. The attenuation of the signal depends on the properties of both the solid formed (viz. the elasticity) and the reaction system.

In this study, zeolite Y seed gel was synthesized as reported in [2] in absence and presence of two different morphology modifying agents (MMA), namely the inorganic lithium carbonate and the organic dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride (TPOAC). It was found that the addition of these MMAs triggers the formation of rotational intergrowth of FAU and its twin structure EMT [3,4], which can significantly increase its catalytic activity as solid base [5] or acid catalyst [3]. Not many techniques allow adequate investigations of the seed gel formation, since no crystalline product is formed in this step yet. However, due to the change in the densities of the gel, the technique of ultrasonic diagnostic allows to observe the course of the nucleation even with different MMAs. Another advantage of using this method is the determination of the necessary aging time with the same experiment.

This contribution shows that the amount of lithium carbonate in the seed gel influences the induction time until the nuclei formation starts. With increasing amounts of Li2CO3, the induction time is extended as the initial attenuation signal is increased. Nevertheless, the course of the ultrasound signal also changes with the amount of lithium carbonate in the gel. The results indicate that a higher concentration of lithium carbonate might increase the concentration of nucleation sites. In comparison, the addition of the organosilane TPOAC slows the nucleation even further down. This study confirms that the different MMAs influence strongly the nucleation as well as the necessary aging time. In addition, it could be shown that the novel method of ultrasonic diagnostic is not only a helpful tool to investigate the crystallization of molecular sieves, but can also be used to investigate earlier steps like the aging of seed gels.

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1134 - RELIABILITY OF FRAMEWORK AL POSITIONS ASSIGNMENTS IN ZEOLITES BASED ON COMPUTATIONAL INVESTIGATION MFI

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Detail knowledge of aluminum distribution in zeolites is perhaps the greatest challenge in the zeolite science today.[1] Neither the distribution of individual Al atoms among the crystallographically independent framework sites nor the relative positions of two framework Al atoms can be obtained from experiments in general (except trivial cases like Al pairs separated by just a single SiO4/2 tetrahedron). Only indirect methods based on numerous assumptions can be used in some cases and the validity of adopted assumptions is often rationalized based on relevant computational investigations.

It is essential to investigate the zeolites at operando conditions, modeling the chemical composition (including molecules present in the zeolite channels) and temperature as close to corresponding experimental situation as possible.[2] Number of assignments of Al positions in MFI has been presented in literature, however, none of them has considered operando conditions. Instead, zeolites were treated at 0 K and the 27Al chemical shieldings were calculated from just a single structure corresponding to minima optimized on potential energy surface (PES). In the case of MFI this is insufficient approach since the PES is very complex with huge number of local minima and probability of finding global minimum is thus very low.

The goal of this study is twofold: (i) compare the performance of various simplified models used for MFI and (ii) present the calculated 27Al shifts for individual T-sites with operando model that also avoids the problem of local minima on PES. We use “Double Machine Learning” (DLM) approach to achieve the goals. DLM is based on long MD trajectory (typically 1 ns) carried out for the system with the same composition as experimental material, including water. It is however, computationally prohibitive to do such calculations on the ab initio level. Instead, we have developed highly accurate reactive neural network potentials (NNPs) that leads to more than 103 computational speed up.[3,4] Chemical shieldings are calculated for the subset of points along the MD trajectory using again simplified formula obtained from ML analysis. This approach was tested on simpler zeolites (CHA and MOR) and provided excellent agreement with experiment.

In brief, character of the charge compensating cation (H and Na) as well as number of water molecules in the vicinity greatly affect the chemical shielding for most of the T-site, however, this effect is far from being uniform. Therefore, operando conditions are essential for Al NMR assignment. Nevertheless, individual positions cannot be recognized, only certain group of sites showing similar NMR characteristics.

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1251 - TUNING FE ACTIVE SITES IN ZEOLITES

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Catalytic decomposition of CH4 and N2O are tantalizing but fundamentally challenging goals, with useful valorization for eergy related and environmental applications. Current technologies based on zeolites deactivate too rapidly for practical application or require too harch conditions to activate. We found that similar active sites hosted in different zeolite lattices can exhibit markedly different reactivity with N2O and CH4 and other properties, depending on the size of the zeolite pore apertures and on the shape of the framework rings. These can be chosen through zeolite framework selection. The structure function relations are derived and demonstrated.

Fe active sites were synthesised in different zeolite frameworks (BEA, ZSM-5, FER, MOR, CHA) and their reactivity with N2O and CH4 was investigated. Intermediates were identified with advanced spectroscopy (UV-Vis, FTIR, Mössbauer, NRVS, MCD, rRaman, EPR) and reaction kinetics were measured with operando UV-vis spectroscopy coupled with mass spectrometry. The results were interpreted and explained using spoctroscopically validated comutational models.

Different zeolite frameworks have differently geometries of the 6-membered rings that host the active alpha-Fe sites.[1] This influences their ability for oxygen atom abstraction from N2O to form highy reactive alpha-O sites.[4] The underlying property is revealed to be a geometric distortion imposed by the zeolite lattice, familiar in enzymatic catalysis as an entatic state. At the same time this disctortion influences the binding energy of the Fe ion in the exchange site,[1,3] and also the reactivity of the alpha-O site in hydrogen atom abstraction from CH4.[2] This creates a trade-off triangle of properties steered by the 6-ring symmetry, that must be optimised to the intended application and reaction conditions.

Also the window size controls reactivity of alpha-O with CH4. Known alpha-Fe zeolite with large pore apertures deactivate completely after a single turnover. New materials with small apertures were found to regenerate 40% of active sites in zeolite after single turnover, enabling a catalytic cycle.[5] Detailed spectroscopic characterization of reaction intermediates and density functional theory calculations show that hindered diffusion through small pore apertures disfavors premature release of CH3 radicals from the active site after C-H activation, thereby promoting radical recombination to form methanol rather than deactivated Fe-OCH3 centers elsewhere in the lattice.

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CATEGORY: SEPARATIONS

1030 - CU EXCHANGED CHA TYPE ZEOLITES FOR H2 D2 SEPARATION

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Chabazite-type (CHA) zeolites have remarkable structural characteristics that make them promising candidates for use in separation and catalytic processes. The CHA framework topology can be described by an arrangement of hexagonal rings, consisting of Si or Al atoms. Rings are stacked in an AABBCC sequence forming a three-dimensional structure with cylindrically shaped cavities connected through eight-membered oxygen rings (8 MR) [1]. In Al-rich (nSi/nAl < 3) CHA-type zeolites, cations can be found in different positions, including the 8 MR windows that divide the cavities. The presence of cations in these sites enables adjustment of the adsorption characteristics by a change in the nSi/nAl ratio and cation type [2]. It has recently been demonstrated that Na-exchanged CHA-type zeolites with nSi/nAl = 2.1 reveal high D2/H2 selectivity with a maximum value of 13 at -233 °C [3]. At the same time, no studies on the separation of hydrogen isotopes on transition metal ion-exchanged chabazites have been reported, while for Cu-based MOF with CHA topology Si et al. demonstrated effective H2/D2 separation in breakthrough experiments at -196 °C [4]. In this study, we present the preparation and characterization of Cu-exchanged CHA-type zeolites and preliminary results of their use in H2/D2 separation. CHA-type zeolites were synthesized via hydrothermal conversion of zeolite Y following the method reported by Bourgogne et al. [5]. 25 g of zeolite Y (CBV400) was mixed with 198.2 mL of the deionized water in the polypropylene bottle. Next, 26.8 mL of 45% wt. KOH solution was added to the bottle. The four of the same mixtures were prepared. Hereafter they were placed in a preheated oven at 95 °C for 4, 9, 12 and 15 days. Afterwards, the solid was washed to remove KOH until neutral pH and dried overnight at 95 °C. The as-synthesized zeolites were desilicated using 30 mL of 0.2 M NaOH (per 1 g zeolite) at 80 °C for 2 hours and the influence on the pore width is investigated. The as-synthesized and desilicated CHA-type zeolites were ion-exchanged in an aqueous solution with anhydrous copper acetate at room temperature for 24 hours with a target Cu2+ loading of 0.7 wt.-%. Characterization of the materials with the respect to their structure, elemental composition, and morphology will be shown. Furthermore, copper (II) species in the framework are characterized by continuous wave electron paramagnetic resonance (CW EPR) and pulse EPR. In situ EPR provide insight into copper – hydrogen isotope interaction for understanding the mechanism of H2/D2 separation using the prepared materials.

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1043 - DIFFUSION AND ADSORPTION OF 2 METHYLPENTANE AND 3 METHYLPENTANE IN SILICALITE 1 CRYSTALS

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Molecular diffusion is often a key criterion for the performance of microporous materials in technological applications [1]. Due to the intimate contact of guest molecules with the inner surface of microporous adsorbents, slight changes in the structure of the guest molecules may already lead to considerable changes in their diffusion behavior. One example of such behavior, which is investigated in this study, is the diffusion of 2-methylpentane (2MP) and 3-methylpentane (3MP) in large crystallites of silicalite-1 studied via IR microscopy (IRM). Furthermore, a rationalization of the observed large differences (factor of 3) in the transport diffusivity of 2MP and 3MP using transition state theory (TST) simulations is attempted.

Silicalite-1 was prepared via a synthesis adapted from Mueller and Unger [2] using Ludox® as silica precursor, aqueous ammonia solution as base and tetrapropylammonium as structure-directing agent. The molar synthesis gel composition was 59:4:123:2280 (SiO2/(TPA)2O/(NH4)2O/H2O). Diffusion investigations were conducted with a Bruker Hyperion 3000 IR microscope attached to a Bruker Vertex 80 FT-IR spectrometer with polychromatic MIR source, Michelson Interferometer and a single element MCT (mercury cadmium telluride) detector. Grand canonical Monte Carlo simulations were carried out using the RASPA2 package [3] using force field parameters from Dubbeldam [4] to predict the single component sorption isotherms. To estimate the self-diffusivity of 2MP and 3MP the dynamically corrected TST method was used [5].

The adsorption isotherms show that 2MP adsorbs more strongly at loadings < 4 molecules per unit cell while the equilibrium loading is higher for 3MP at loadings > 4 molecules per unit cell. The experimental data obtained is in good agreement with grand canonical Monte Carlo simulations. Additionally, the loading dependent transport diffusivities were studied. The transport diffusivity only marginally increases below a loading of 4 molecules per unit cell, but strongly increases for a higher loading in the case of both 2MP and 3MP. While the trend observed for both molecular probes is the same, the transport diffusivity of 2MP is 2.0 – 4.5 times higher than that of 3MP. This is attributed to lower energy barriers for 2MP mobility, differences in the energy profiles and the orientation of both molecules inside the pore system with the help of molecular simulations.

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1062 - DIFFUSION OF SUGAR ALCOHOLS MONO AND DISACCHARIDES IN ZEOLITE NA Y

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The knowledge of diffusion coefficients within zeolitic micropores is a prerequisite for understanding chromatography, adsorption and catalysis [1]. Only a few studies are devoted to the diffusion of sugars and sugar alcohols in zeolite crystals [2-5]. The present work is based on chromatographic experiments with a HPLC column (125 mm x 4.6 mm) filled with an industrial zeolite NaY (powder, dcrystal = 5 µm). The eluents were water and mixtures of water with acetonitrile. Due to the hydrophilic nature of the zeolite surface, the liquid inside the micropores is mainly water while the remaining water-acetonitrile solvent flows between the zeolite crystallites. Different retention times result from the distribution between water and the organic solvent-water phase and both the interaction of the solute with the inner micropore surface. The separation principle may be regarded as a particular kind of hydrophilic interaction chromatography (HILIC).

A range of different hydroxy compounds was injected and the peak shape was analyzed via the second central statistical moment M2 [6]. The second moment M2o of molecules, which are too large to enter the micropores, are used for the determination of the axial dispersion characterizing the liquid flow between the crystallites. Molecules bearing M2 >> M2o can then be analyzed with respect to their apparent intracrystalline diffusion coefficient. The diffusion coefficient of sugar alcohols decreases with their molecular weight when recorded over a broad range of temperatures (15 – 90 °C). Remarkably, inositol (6-ring) diffuses less rapidly than sorbitol which is the acyclic form of inositol.

The interpretation of the peak shapes originating from monosaccharides is impeded by the fact that tautomerization resulting in a mixture of 6-ring and 5-ring forms including α- and β-form may cause up to four separate or one broad peak [7]. The second central moment can therefore be interpreted as tautomerization rate [8] and/or diffusion [6]. The second central statistical moments of disaccharides were found to differ too due to their isomers. Owing to their molecular size, the disaccharides require temperatures exceeding 80 °C to generate broad symmetric peaks.

Sucrose was also adsorbed via batch adsorption, thus, reducing the specific micropore volume. However, compared to adsorption in a hydrophobic dealuminated zeolite Y [5], the sorption at room temperature is very slow. An electrostatic effect may therefore be the reason that HPLC of disaccharides requires high temperatures.

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1290 - TRANSIENT ANALYSIS OF PROPYLENE AND PROPANE PERMEATION THROUGH AG X MEMBRANE

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Olefin is an important raw feedstock in the petrochemical industry. Since olefin is produced with paraffin, olefin requires separation from paraffin. Currently, olefin is purified by cryogenic distillation, which consumes huge energy. A more energy-efficient membrane separation method has been attracting attention. We have developed a separation membrane, membrane of Ag+ ion-exchanged X-type zeolite, Ag-X membrane, based on the difference in affinity between membranes and olefin. We have previously found that Ag-X membrane exhibits a high olefin selectivity for olefin/paraffin separation [1]. However, the detailed mechanism of separation is still an open question. In this study, we focused on the permeation behavior of C3H6 through Ag-X membrane and carried out transient response experiments using Q-MS.

Na-X was synthesized on the outer surface of tubular Al2O3 support by a secondary growth method. Ion exchange for Na-X membrane was conducted to obtain Ag-X membrane.

We performed permeation tests using propylene isotopes, C3H6 and C3D6, to study C3H6 permeation behavior through Ag-X membrane. After C3D6 was adsorbed on Ag-X membrane, Ar was supplied to purge the system to remove C3D6 in the gas phase, and then C3H6 was fed. The permeant was monitored by using Q-MS throughout the experiment. After confirming the disappearance of C3D6 after the Ar purge, we supplied C3H6 to the membrane and observed the appearance of C3D6 desorption peak. Such desorption of C3D6 accompanied by the supply of C3H6 suggested that strongly adsorbed C3D6 remained in the membrane and hardly desorbed in Ar atmosphere. The amount of C3D6 desorbed during C3H6 supply was consistent with the amount of strongly adsorbed C3H6 measured in the adsorption test.

Further, we carried out a similar transient response experiment using C3H6 and C3H8 to understand the contribution of each molecule to the selectivity through Ag-X membrane. After C3H6 was supplied and adsorbed on Ag-X membrane, Ar was supplied to purge the gas phase, and then C3H8 was fed to the membrane. In this case, whereas the desorption peak of C3H6 appeared during the Ar purge, that of C3H6 was hardly observed when C3H8 was fed, suggesting that the strongly adsorbed C3H6 could not be desorbed by C3H8. These results indicate that C3H6 strongly adsorbed on Ag-X membrane inhibited the adsorption and permeation of C3H8. This behavior seemingly contributed to the high selectivity for C3H6/C3H8 separation using Ag-X membrane.

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CATEGORY: STRUCTURE CHARACTERIZATION

1026 - CHARACTERIZATION OF NATURAL ZEOLITES OF ARMENIA GEORGIA AND KAZAKHSTAN AND THEIR THERMALLY MODIFIED FORMS

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Nowadays natural zeolites are the widest using sorbents for removal many types of harmful pollutants from wastewaters due to their high sorption capability, availability and low-cost. The objects of our study are natural zeolites from the Nor Kokhb deposite, Armenia, the Rkoni plot of the Dzegvi-Tedzami deposite, Georgia, and the Chankanay deposite, Kazakhstan, selected for the preparation of new bactericidal zeolite filter materials for purification and disinfection of water from various sources [1].
According to the results of chemical analysis and XRD data, the zeolite from the Nor Kokhb deposit is a typical calcium clinoptilolite (Si/Al=5.12) also containing 7% of kanemite (HNaSi2O5·3H2O), 5% of quartz, 4% of natrolite ([Al6Si6O24]-SOD) and 3% of sigma-2 zeolite ([Si64O128]-SGT); the sample from the Rkoni plot is a high-silica heulandite (Si/Al=3.6) mixed with a small amount (≈10%) of chabazite (Si/Al=2) and containing relatively high content of sodium exchangeable ions; zeolite from the Chankanay deposit is a mixture of heulandite (≈40%), chabazite (≈40%) and quartz (≈20%) containing relatively high content of calcium ions. The presence of a developed system of micropores is confirmed by the FTIR spectra, the low-temperature adsorption-desorption isotherms of nitrogen correspond to the filling of micropores (Langmuir plot) at low relative pressures (p/po<0.3) and demonstrate a hysteresis loop with a jump at p/p0= 0.4-0.5 indicating the presence of mesopores. The Armenian clinoptilolite is characterized by relatively large BET surface area (19.4 m2/g), the pore size distribution dV/dD curves show a sharp maximum at 4 nm in diameter and a broad distribution of mesopores in a range of 20-60 nm; the distribution of mesopores in Georgian heulandite (12.8 m2/g) has a maximum at 12 nm, while distribution of mesopores in Kazakhstani heulandite (2.75 m2/g) has two broad maxima at 6 and 50 nm.
Powder XRD patterns of samples calcined at different temperatures (100 – 800 oC) and data of thermal analysis (TG/DTA/DTG) show the stability of the crystalline structure in clinoptilolite up to 720 oC, the heulandite phase in Georgian and Kazakhstani samples begins to break down at temperatures over 200 oC, and the chabazite phase is stable up to 830 oC. The BET micropore surface area in Armenian clinoptilolite and Georgian heulandite decreases with an increase in the calcination temperature, while in the Kazakhstani heulandite it increases and reaches its maximum value (7.36 m2/g) after calcination at 800 oC, when the heulandite phase is completely decomposed. The total volume of pores varies nonmonotonically and insignificantly, in Armenian clinoptilolite from 0.056 cm3/g (after calcination at 600 oC) to 0.077 cm3/g (700 oC), in Georgian heulandite from 0.078 cm3/g (700 oC) to 0.093 cm3/g (100 oC), in Kazakhstani heulandite it reaches a maximum value (0.087 cm3/g) after annealing at 700 oC and a minimum value (0.071 cm3/g) after annealing at 800 oC. As for the pore size distribution, the diameter of nanosized pores (4-12 nm) in all samples tends to decrease with increasing heat treatment temperature, the diameter of mesopores (50 nm) in Kazakhstani heulandite generally increases, and the distribution of mesopores in Armenian clinoptilolite changes in a complex way. Thus, the porous structure of the investigated clinoptilolite and heulandites is very sensitive to the heat treatment of the samples.

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1126 - INFLUENCE OF WATER VAPOR TREATMENT FOR NH3 TPD ON ZEOLITES

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Temperature programmed desorption of ammonia (NH3-TPD) is commonly used to evaluate the acidity (acid amount, acid strength) of solid acid catalysts such as zeolites. In many cases, there are two peaks, l-peak (low temperature) and h-peak (high temperature) in the TPD spectrum.

The l-peak is derived from ammonia molecules which are adsorbed by hydrogen bonding on NH4+ cation on acid sites and is not considered to indicate the acidity. However, in the case of zeolites with weak acidity, such as Y-type zeolites, the l-peak and h-peak overlap, making it difficult to evaluate acidity. NH3 TPD measurement with steam treatment is considered being effective to eliminate the l-peaks. In this contribution the procedure, and precautions are described. Ammonia as probe molecule is adsorbed onto the zeolite sample until it reaches equilibrium. Then the temperature of the sample is continuously increased, causing an enrichment with the desorbed molecules in the inert carrier gas (Helium). The standard TCD (Thermal Conductivity Detector) measures the total adsorbed amount and not the specific desorbed constituents. However, since zeolite adsorbs water in its pores, it is necessary to use a detector that can detect water and ammonia separately when measuring TPD. Also, since water vapor is introduced at high temperature, this method is not applicable to samples whose properties are changed by water vapor.

Therefore, a quadrupole mass spectrometer is used to detect the desorbing ammonia at mass number 16. Mass number 17 was not used because the peak at 17 can be affected by the desorbed water.
NH3-TPD measurements were performed under the following conditions.
Measuring equipment : BELCAT II + BELMASS
Sample : MFI, 50 mg
Temperature ramp rate and target temperature : 10°C/min, 610°C
Adsorption gas : NH3/He 5%

According to Igi et al [1], in their experiments the steam treatment was performed by repeating the evacuation of the sample cell with following steam introduction. Differently, the catalyst analyzer BELCAT II is a dynamic flow type equipment operating permanent at atmospheric pressure. Fully saturated water vapor is generated by an advanced bubbling method with inert gas at room temperature under atmospheric pressure.
The experimental results show that steam treatment eliminates the l-peak and leaves the h-peak shape almost unchanged, indicating that steam treatment in NH3-TPD measurement is very effective for eliminating the l-peak and examining the h-peak in detail. To perform NH3-TPD measurement with BELCAT II, the vapor option and a quadrupole mass spectrometer BELMASS is necessary.

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1229 - SINGLE ATOM RU ON ZEOLITE CATALYST FOR THE VALORIZATION OF MUCONIC ACID VIA ISOMERIZATION AND HYDROGENATION REACTIONS

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Muconic acid (MA) is a high value-added product that can be present in 3 isomeric forms: cis,cis (cc), cis,trans (ct), and trans,trans (tt). Its added-value is attributed to its high potential as a starting material for the synthesis of value-added derivatives such as (1) adipic acid via hydrogenation reaction, (2) hexenedioic acid via mono-hydrogenation, and (3) terephthalic acid via Diels-Alder cyclo-addition (Figure 1) [1]. For the products (1) and (2), any of the isomers can perform the hydrogenation reaction, however, the tt-isomer is preferred due to its stability against the intramolecular lactonization reaction that occurs on the two other isomers. While for product (3), the tt-geometry is primordial to performed the Diels-Alder cycloaddition. In the recent years, biotechnological processes have been developed to produce both ccMA and ctMA from biomass-derivatives, however, to access the value-added derivatives, an isomerization step allowing the formation of tt-muconates from either cc or ct-muconates must be developed. In this work we present a single-atom Ru on Beta zeolite catalysts to investigate the isomerization of ct-muconates. In addition, the single-atom Ru on zeolite catalysts will be also tested in the mono-hydrogenation of MA to produce hexenedioic acid (2).

To achieve atomic dispersion of Ru on Beta zeolites (12.5 < Si/Al < 250), Ru was loaded via cation exchange method using the RuIII(NH3)6Cl3 precursor. The amount of added Ru was estimated to the equivalence amount of strong Bronsted acid sites on the zeolites. The activation conditions were primordial to achieve both isomerization and hydrogenation activities. In that sense, the thermal dissociation of the NH3 ligands was followed and optimized activation temperatures were found between 300 and 350°C, where only 1-2 out of the 6 NH3 ligands remain attached to Ru (EXAFS confirmation) [2].

Isomerization: 95% selectivity towards the tt-isomers could be achieved together with high productivity values (up to 85 g/L.h) and TON >2500 mol/mol. In addition, deep characterization were performed (EXAFS, ICP, H2-TPR, FT-IR, BET) to confirm the atomic distribution of Ru and elucidate the reaction mechanism. Finally, one-pot isomerization/Diels-Alder reaction was conducted to produce (3) after a full conversion of ct-muconates. This reaction was also proven to be applicable to various di-alkyl muconates.

Hydrogenation: To date, the synthesis of (2) was only reported using electrochemical methods [3]. Hexenedioic acid can serve as a co-monomer in the synthesis of nylon-6,6 polymer, which opens routes for the functionalization of the produced polymer with chemical reactions on the remaining C=C double bonds. The difficulty in making (2) remain in the control of the hydrogenation step which usually end up with the formation of (1) after excessive hydrogenation. In this part, we present a new method to access (2) from MA and muconates using Ru-Beta catalysts in an H2-free system using ethanol (solvent) as a hydrogen source. The desired product (2) was obtained in yields surpassing the 50% and selectivity around 70%. The optimization of the reaction conditions to achieve will be discussed in this communication.

1237 - HYDROPHOBICITY AND VAPOUR ADSORPTION STUDIES OF ZEOLITIC IMIDAZOLATE FRAMEWORKS

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Introduction

Zeolitic imidazolate frameworks (ZIFs), are a class of metal-organic-frameworks (MOFs) consisting of metal ions connected by imidazole linkers. ZIFs are commonly used as adsorbents due to their high surface area and ability to tune pore size. It is possible to measure the amorphous content and water uptake by analyzing vapor sorption using DVS (Dynamic vapor Sorption) experiments. Co-sorption measurements with VOCs (Volatile Organic Compounds) under humid conditions can be used to compare powder equivalent samples to analyze their efficiency.

Experimental

All samples were synthesized at Imperial College London using chemicals with a minimum purity of 99% purchased from Sigma Aldrich. Powder forms of ZIF-8 and ZIF-67, monolithic absorbents with single modulating ligands ZIF-8 (NB) and ZIF-67 (NB), and monolithic absorbents with multiple modulating ligands ZIF-8 (ML) and ZIF-67 (ML) were all synthesized1.

In the Dynamic Vapour Sorption (DVS) technique a saturated carrier gas flows over a sample. As the sample is exposed to the vapor molecules, the mass will change. As the vapor concentration increases, more vapor molecules are present, and the sample shows an increase in mass. The sorption isotherms can then be plotted by using the mass data against the relative vapor pressure of the solvent. Single-component experiments using water or organic vapor molecules as well as a combination of both components water and organic vapor have been studied.

Results & Discussion

Figure 1 Methanol sorption isotherms. DVS was used to measure the effect of amorphous content on the adsorption hydrophobicity of ZIF monoliths. The inflection point in the methanol curve (Type V isotherm) can be linked to the polarity of the solvent molecule.

ZIF-8 and ZIF-67, similar to high-silica zeolite Y, have a ‘hydrophobic force field’ around their apertures, preventing polar molecules from adsorbing inside without sufficient driving force.

Figure 2 Plot for powder ZIF-8 shows the influence of adsorbate chemistry on the selectivity of the adsorption

Conclusions

Vapor adsorption isotherms show that amorphous content results in increased water uptake. ZIFs have higher surface and adsorption hydrophobicity than traditional nonpolar adsorbents. Co-sorption measurements with toluene, under humidity, find that monolithic ZIF samples outperform powder equivalents, with the mixed-modulator ZIF-67 monolith capturing 28% more VOC compared to the powder ZIFs studied due to its superior volumetric efficiency.

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1241 - INFLUENCE OF SOME CATIONS ON THE ACID STRENGTH OF HIERARCHICAL MORDENITE

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Mordenite is generally considered to be a one-dimensional channels zeolite. It is widely used in catalysis and in separation and purification because of its uniform, small pore size, high internal surface area, flexible framework, chemically and thermally stable porous material. The major drawback of mordenite and zeolites in general is the limited size of the channels and cavities and the lack of interconnectivity. This imposes diffusional limitations of the reactants and products, with large impact on catalysts activity, selectivity, and stability [1].
Hierarchization of zeolites has been proposed as a strategy to efficiently reduce the length of internal diffusion pathways and thus increase the efficiency in catalysis. We have obtained hierarchically structured zeolites with a ratio of Si/Al nearly to 10 in two different ways: by direct synthesis using surfactants as soft templates (MOR-CTAB) and via post synthesis treatment of microporous mordenite using NaOH solution followed by acid washing with HCl solution (MOR -B-A) and calcination. In order to see the influence of the way of preparation on their acid strength as well as fine tuning between Brønsted and Lewis acid sites, both samples were modified by wet impregnation (ion exchange and thermal treatment) with transition metal salts (including nitrates and acetates of Ni2+, Co2+, and Cu2+). The number (density) and strength of the acid sites largely determine the activity and selectivity of the catalysts toward certain reactions such as MTO (conversion of methanol to olefins), methane dehydroaromatization, isomerization, conversion of glycerol to olefins, etc. Usually, the interaction between the acid sites and the basic probe molecules (e.g. acetonitrile, pyridine) is studied to determine their amount and strength, using desorption FTIR spectroscopy under vacuum. The chemical coordination of the metal cations was examined using DRS UV/Vis spectroscopy.

The results show that there is a significant difference in the mesoporosity of mordenite prepared by different methods. On the other hand, the incorporation of the exchangeable metal cations (Ni2+, Co2+, and Cu2+) into the mordenite significantly changes the ratio between the number of probe molecules (deuterated acetonitrile) adsorbed on Brønsted and Lewis acid sites. Different post synthesis treatments, such as wet impregnation with certain metal cations and subsequent thermal treatment, represent powerful tools for fine tuning the strength of acid sites in many zeolites, including mordenite.

Acknowledgment

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1274 - CHARACTERIZATION OF ZEOLITES USING HYDROGEN AND OXYGEN ADSORPTION WITH A PARTICULAR FOCUS IN ULTRA MICROPORES

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Argon and nitrogen are the most frequently used gases to quantify the pore volume and pore size distribution of zeolites by adsorption studies. We have demonstrated previously that oxygen is well suited as an alternative adsorptive to determine pore size distribution on carbon samples. [1] Oxygen has a quadrupole moment about 3.5 times lower than nitrogen and thus the possible effect of polar surface sites is much smaller on the isotherms of oxygen than nitrogen. Furthermore, oxygen has a wide liquid-vapor coexistence curve (54-155 K) that allows for using various cryogenic baths including standard liquid nitrogen.

When it comes to ultra-microporous zeolites such as Chabazite and molecular sieve 5A, kinetic restrictions at cryogenic temperatures (77K, 87 K) limit the use of Ar, N2, and O2 as adsorptive to the extent that the achievement of an equilibrium state cannot be realized. A well-known adsorptive to analyze ultra-micropores in carbons is carbon dioxide at 273 K. [2] Due to the relatively high analysis temperature and the high saturation vapor pressure of CO2 at that temperature diffusion is much faster and pores as small as 4 Å are accessible. For the analysis of materials with polar surface groups such as zeolite, however, the use of CO2 as probe gas is not recommended because of the high quadrupole moment of CO2.

We introduced the use of hydrogen at 77 K as adsorptive for ultra-micropore analysis in pores carbon samples in previous publications. [3, 4, 5] In this work, we extend the use of hydrogen to zeolite samples by introducing new NLDFT kernels.[6] We apply hydrogen in combination with oxygen at 77 K. The H2 molecule has a smaller diameter than O2 and diffuses faster into ultra-micropores, reducing the time of isotherm measurement. Moreover, we show that the dual gas analysis method can be used with O2 isotherm measurements omitting low-pressure points, making the analysis faster.

1289 - X RAY ABSORPTION AND EMISSION SPECTROSCOPY FOR STRUCTURE ANALYSIS OF FE SUBSTITUTED ZEOLITES SYNTHESIZED BY MECHANOCHEMICAL METHOD

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Mechanochemical (MC) reactions have been widely used to synthesize amorphous oxides. It has been reported that metal atoms are uniformly dispersed in the zeolite framework when metallosilicate obtained by the MC method is used for zeolite synthesis [1]. In this study, we investigated the mechanism of zeolite synthesis using the MC method from the viewpoint of the local structure of the heteroatoms. Here, the chemical state and local structural changes of heterometallic species (Fe) during MC and hydrothermal reactions were traced by X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES).

The X-ray diffraction patterns of the synthesized samples showed halo peaks derived from fumed silica and diffraction lines of α-FeOOH. α-FeOOH diffraction intensity decreased with MC reaction time, indicating that amorphization progressed. The Fe K-edge XAFS spectra changed with MC reaction time, showing a significant increasing trend in the intensity of the pre-edge peak around 7107 eV. The pre-edge peak is a transition associated with the d orbital, and its intensity depends on the magnitude of hybridization between the Fe3d and O2p orbitals [2]. In FeO6 octahedra such as α-FeOOH, the point group is attributed to Oh, and Fe3d and O2p cannot hybridize. On the other hand, in the case of FeO4 tetrahedra with Fe substituted in SiO2, the point group is attributed to Td and can be hybridized. Therefore, the pre-edge peak intensity can be regarded as a substitution degree of Fe in SiO2 by the MC reaction. The intensity of the pre-edge peak observed in this study increased after 24 hours of reaction (24 h) compared to before the reaction (0 h), suggesting that Fe was solid-soluble in SiO2 by the MC reaction.

The change of Fe local structure with hydrothermal treatment time was investigated from XAFS spectra of MWW-type zeolite synthesized by hydrothermal method using MC preparation precursor. The results showed that the spectral change with heat treatment time was small, suggesting that the local structure in the precursor and zeolite framework remained almost the same. On the other hand, in the MWW-type zeolite obtained by hydrothermal synthesis using a-FeOOH, the coordination number of Fe changed significantly with hydrothermal treatment time, suggesting that Fe was incorporated while changing the local structure. These results indicate that Fe incorporated into SiO2 as a precursor by the MC method forms the framework structure of zeolite while maintaining the local structure of the precursor.

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1297 - THE ROLE OF TEMPERATURE IN P INDUCED CRYSTAL FLUID INTERACTION A STUDY ON LAU AND HEU TOPOLOGIES

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Natural zeolites can be found in soils, oceanic basalts as well as sediments and diagenetic environments. Their peculiar reversible hydration property (i.e., the ability to adsorb and release H2O molecules) and the ability to overhydrate under pressure, make them suitable carriers of fluids in the upper Earth crust during the early stage of subduction. Despite the extensive study of high-pressure and high-temperature behavior of natural and synthetic zeolites over the last decades, few studies have yet combined the effects of both conditions. Experiments at combined high pressure and high temperature might provide valuable insights on the crystal-fluid interaction preocesses occurring in nature at the geological conditions of stability of zeolites, especially when these microporous compounds can act as carriers and moderators of the circulating fluids.

In this study, the in situ combined high-pressure and high-temperature behavior of two commonly occurring natural zeolites, heulandite and laumontite, was investigated. The P-induced crystal-fluid interaction of these two zeolites was studied at ambient-T by Comboni et al. [1] for laumontite and Seryotkin [2] for heulandite. These results have been used as benchmarks to evaluate the role of temperature on the crystal-fluid interaction. In-situ, HTHP single-crystal synchrotron X-ray diffraction experiments were conducted using a diamond anvil cell (DAC) surrounded by a resistive heater at the ID15b beamline at the European Synchrotron Radiation Facility in Grenoble (France). The setup allowed to reach temperatures of about 150(2)°C. Pressure was measured using the ruby fluorescence technique while temperature was monitored using a thermocouple located very close to the P-chamber, allowing a precise determination of both these variables. The results obtained were consistent with those calculated using the Au-powder pattern.

The results showed that temperature significantly increased the kinetics of H2O adsorption in laumontite, with respect to the compressional behavior at room conditions, leading to a volume expansion observable already at pressures < 5 kbar. It was previously found that laumontite hydrated at ambient conditions after 24 hours, while the presence of a temperature gradient reduced the time at about 15 minutes. Even for heulandite, the comparison with literature data suggests that a higher H2O adsorption rate was observed when the thermal gradient was applied.

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1345 - FLY ASH DERIVED ZEOLITES AS POTENTIAL SORBENTS FOR ELEMENTAL MERCURY REMOVAL FROM SIMULATED GAS STREAM

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The fly ash produced as waste in the process of conventional coal combustion was utilized in hybrid synthesis of zeolites X and A from Faujasite (FAU) and Linde Type A (LTA) frameworks, respectively. Applied synthesis method included modification together with crystallization stage. The sorbents modification was performed by introducing metals into zeolites structure in order to create ability to form stable bonds with elemental mercury (Hg0). Mercury constitutes a hazardous threat, due to its high chemical and biological activity, durability, volatility and susceptibility to migrations over long distances from the source of pollution. According to the Agency for Toxic Substances and Disease Registry, mercury is placed third on the list of substances most hazardous to human health [1]. In countries where heat or electricity production is still based on the processes of fossil fuel combustion, a significant amount of mercury is released into the atmosphere, along with the exhaust gases from power plants. It is important that, to date, the interaction between mercury (occurring in exhaust gases) and the investigated/tested sorbents, as well as the mechanisms governing the bonding processes, which are still not well-recognized, remain in the domain of research and exploration and require further in-depth studies. Therefore, there is a need to carry out research in this area. The use of waste in form of fly ash as a source of silicon and aluminum as well as the proposed method of zeolite synthesis fits the circular economy idea [2].

The effect of zeolites modification on Hg0 removal from simulated gas stream was studied empirically using prototype installation designed to test the effectiveness of sorption by solid state sorbents. Both derived zeolites X and A modified with silver nitrate revealed significant mercury uptake during 150-minutes sorption experiment. The amount of elemental mercury removed in experiment ranged from 5.69 to 6.01 µg Hg0/1g of sorbent for zeolites X and from 4.47 to 4.86 µg Hg0/1g of sorbent for zeolites A. In order to confirm the effectiveness of the sorbents towards mercury bonding, the possible re-emission effect was tested as well. Derived zeolites X and A did not show mercury re-emission after the sorption process, which confirms stable bonding of Hg0 in the structure of synthesized zeolites. The proposed hybrid synthesis method possesses the potential to be implemented for both fly ash utilization as well as the time and energy saving production of aluminosilicate, porous materials with high Hg0 removal efficiency. This research was supported by National Science Centre, Poland, grant no 2021/41/N/ST5/03214.

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1163 - TRANSFORMATION OF FRUCTOSE TO HMF - THE IMPACT OF BRØNSTED ACID SITE LOCATION IN SBA-15 MATERIALS

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Catalytic processes based on the use of solid acid catalysts are very important for production of a great variety of valuable substances. Currently, an interesting global challenge is the catalytic processing of (hemi)cellulosic streams, obtained from lignocellulosic resources, in biorefineries, for the production of valuable chemicals and biofuels. In particular, the catalytic conversion of cellulose-derived sugars into furanic building blocks (i.e. HMF) from hexoses has received tremendous attention due to their vast functional versatility, even being described as a sleeping giant in the sector of renewables [1]. These processes involve substrates and products of rather bulky character. Therefore, the application of solid catalysts having a well-defined porous structure can improve the diffusion to/from the active centres. In this study the mesoporous material of SBA-15 type was applied for the immobilization of 3-(trihydroxysilyl)-1-propanesulfonic acid (TPS) or (3-mercaptopropyl)trimethoxysilane (MPTMS) solely inside the pores of the support as well as both inside the pores and on the external surface of SBA-15.

SBA-15 was prepared via conventional hydrothermal method like that described in [2]. Prior to organic template removal, i.e. Pluronic P123, a part of the support was modified by hexamethyldisilazane (HMDS) in order to block silanols on the external surface of the material similarly as in [2]. After this procedure the template was removed by extraction in Soxhlet apparatus using methanol as a solvent. The same method of Pluronic P123 removal was applied for the material unmodified with HMDS. The resulted samples were further functionalized with TPS or MPTMS species. In the functionalization with the latter modifier, hydrogen peroxide was used to oxidize thiol species to sulphonic ones.

Successful synthesis of SBA-15 was confirmed by XRD as well as by low temperature N2 adsorption/desorption measurements. The mesoporous structure was not affected by the modification with HMDS, TPS or MPTMS, which was corroborated by HR-TEM. The efficiency of TPS and MPTMS incorporation was estimated by elemental analysis, whereas the XPS data allowed to follow the efficiency of thiol species oxidation. The pyridine adsorption followed by the FTIR measurements pointed to a higher number of Brønsted acid sites in the samples in which silanol groups were not blocked on the outside surface of SBA-15. This feature has an impact on a higher activity of these materials in fructose transformation to HMF, however, the location of acidic sites solely inside the pores of SBA-15 led to a decrease in levulinic acid formation, which, in turn, allowed increasing HMF selectivity. The influence of the number of acidic sites and their different location in SBA-15 on the transformation of fructose will be described in details.

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1359 - RECOGNIZING THE MINIMUM STRUCTURAL UNITS DRIVING THE CRYSTALLIZATION OF SAPO-34 FROM A TOP-DOWN PROCESS

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Zeolites and their analogs SAPO molecular sieves are important industrial ion-exchangers, adsorbents and catalysts, thanks to their regular microporous crystalline structure, suitable acidity and excellent (hydro)thermal stability. Considerable efforts have been made to understand their nucleation and crystal growth with the aim to realize rational synthesis and property tailoring. Unfortunately, the hydrothermal reaction condition is very reactive, and the reactant mixtures present heterogeneous nature where gel, supersaturated solutions, amorphous solid phase, crystals and even aggressive liquids are involved.1 The crystallization course happens in a black box, which raises the difficulties in monitoring the evolution of crystallization process. What is the amorphous precursor like at the critical point before crystallization acceleration, and what is the most critical structural units to fasten the crystallization of target zeolite remains elusive.

SAPO-34 molecular sieve, as an important industrial catalyst for the methanol-to-olefins (MTO) process, has attracted tremendous attention.2 Many synthetic strategies, including top-down recrystallization3, mesoporogen and/or seeds assistance, have been developed to control the crystallinity, crystal morphology and composition so that its catalytic efficiency can be further improved. The principal idea for the regulation of crystallization and morphology is to make the SAPO-34 crystal nuclei extremely prosperous while inhibiting or interfering crystal growth. Nevertheless, the crystallization mechanism of SAPO-34 is still far from well understood and tremendous trial and error experiments are inevitable. It is thus highly desired to figure out the exact driving force of provoking the crystallization of SAPO-34.

In this work, we established a simple top-down reconstruction system where amorphous ball-milled SAPO-34 was recrystallized under the assistance of single organic amine solution.4 The complex evolution process, generally involved the dissolution of inorganic sources and the subsequent nucleation, were therefore simplified so that the crystal growth process was directly correlated to the organic structure-directing agent (OSDA) type and reaction conditions employed. Moreover, a transparent precursor solution was prepared in this study, which could recrystallize rapidly to yield small SAPO-34 crystals. The components and structures of the liquid phase were identified by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), solid-state MAS NMR and atomic pair distribution function (PDF) analyses. The minimum structural units effective for driving the rapid crystallization of SAPO-34 were determined at an atomic level, which would provide rational guidance on seed selection for synthesis control and properties tailoring of SAPO molecular sieves.

1128 - ADVANCED X-RAY CHARACTERIZATION OF ZEOLITES

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Porous materials such as zeolites are often characterized by X-ray scattering and diffraction methods such as small-angle X-ray scattering (SAXS) and X-ray diffraction (XRD). X-ray based methods are advantageous over complementary methods such as electron microscopy due to the minimum need for sample preparation, the non-destructive nature of X-rays and the possibility to work under either ambient or non-ambient conditions. Non-ambient conditions can include high or low temperatures, humidity, reactive gases, electrical load, or a combination of these variables. Anton Paar produces state-of-the-art XRD and SAXS systems for the laboratory, in addition to a wide range of non-ambient attachments that enable a huge variety of such experiments to be performed.

With Anton Paar's SAXSpoint 5.0 instrument, small- and wide-angle X-ray scattering (SAXS/WAXS) experiments in both transmission and grazing geometry (GISAXS/GIWAXS) are possible. With the SlideMasterTM moving detector feature, automatic SAXS and WAXS measurements without manual user interaction are possible. A large variety of sample holders allowing for non-ambient measurements are available that allow e. g., for in situ experiments of water uptake at specific levels of humidity either in zeolite powders or thin-film phases. With high temperature stages that can be operated either in vacuum or in specific atmospheres, processes such as template removal to generate open, porous structures can be studied.

XRDynamic 500 is the ground-breaking automated multipurpose powder X-ray diffractometer from Anton Paar. It features the patented TruBeam™ concept which comprises a large goniometer radius and evacuated optics units, automatic change of the beam geometry and X-ray optics, and automated instrument and sample alignment routines. These combine to deliver outstanding data quality (in terms of resolution, signal-to-noise ratio, and low angle data) that can be measured with high efficiency. XRDynamic 500 is suitable for powder XRD (in reflection and transmission), grazing incidence XRD (GIXRD), non-ambient XRD, PDF analysis, SAXS and more. A wide variety of sample stages and sample holders ensures that there is an optimized instrument configuration available for all types of measurements. This includes specialized set ups such as the XRK 900 reactor chamber where measurements can be performed at temperatures of up to 900 °C, 10 bar pressure, and under reactive gas conditions (static or dynamic) to simulate real world reaction conditions.

Using both XRD and SAXS together in combination with other methods can give complementary information which allows a more in-depth understanding of the sample in question and its properties. We will show recent data on porous materials such as zeolites measured by both SAXS and XRD to highlight the potential of such measurements in the lab.

CATEGORY: ON THE WAY TO UTILIZATION

1379 - PREPARATION OF TIO2/ZIF-8 HYBRID MATERIAL, CHARACTERIZATION AND TESTING OF ADSORPTION AND PHOTOCATALYTIC PROPERTIES FOR IMIDACLOPRID REMOVAL

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According to a recent report, imidacloprid (1-(6-chloro-3- pyridylmethyl)-N-nitroimidazolidin-2- ylideneamine) is among the 14 banned pesticides still widely used in some EU member states [1]. It is expected that the consumption of neonicotinoids will continue to increase in the coming years, as the banned neonicotinoids are likely to be replaced by those still approved. Therefore there is great need for the development of technologies for efficient removal of agricultural pollutants present in soil and water ecosystems. In the last decade, metal-organic framework materials (MOFs) have received considerable attention as a research focus in both adsorption and photocatalysis [2]. This is due to the great chemical and functional adaptability of MOFs resulting from the use of different organic ligands, metals, and metal clusters, as well as different preparation methods and crystallization conditions. The aim of this study was to develop hybrid TiO2/ZIF-8 photocatalysts and evaluate their activity for imidacloprid removal. The hybrid photocatalysts were prepared by an innovative method involving hydrothermal synthesis at 150 °C using a mechanochemically synthesized zeolitic imidazolate framework (ZIF-8) and titanium tetraisopropoxide as titanium dioxide (TiO2) precursor [3]. Three composite photocatalysts with different mass fractions of titanium dioxide (5, 50, and 95 wt%) were synthesized and characterized, and their adsorption and photocatalytic properties for the removal of imidacloprid were investigated. Various instrumental techniques such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), UV/Vis spectroscopy, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and the laser diffraction were used for detailed characterization of the prepared samples. The study of adsorption and photocatalytic properties was performed in a suspension reactor, using a Pen Ray UVA lamp (365 nm) during photocatalytic measurements. The degree of degradation of imidacloprid was monitored by high performance liquid chromatography (HPLC). The equilibrium adsorption test showed that ZIF-8 is a good adsorbent and can adsorb 65% of the model component under the working conditions used in this work, while the hybrid photocatalysts can adsorb 1-3% of the model component. It is assumed that the adsorption is hindered by the TiO2 layer on the surface of ZIF-8, which blocks the interactions of ZIF-8 and imidacloprid. A significant decrease in band gap energies (3.1-3.6 eV) was observed for the hybrid TiO2/ZIF-8 photocatalysts compared to the values obtained with ZIF-8 (5 eV), depending on the mass fractions of TiO2. The highest removal efficiency of imidacloprid was achieved with the hybrid photocatalysts containing 5 wt% TiO2. The high stability of the photocatalyst was achieved under the specified operating conditions. Although the prepared hybrid photocatalysts showed only moderate and still insufficient activity, we believe that this work provides useful guidelines for the design and development of new hybrid photocatalysts with great potential for visible light application for environmental remediation.

References

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CATEGORY: DECARBONIZATION AND CO2 MANAGEMENT

1090 - CHANGES IN CO2 ADSORPTION KINETICS ON NANO-SIZED ZEOLITES SYNTHESIZED USING ALKALINE EARTH METAL CATIONS

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Zeolites are microporous solids possessing molecule-sized systems of channels and cages containing extraframework cations. These characteristics confer remarkable properties which has led to their application in key adsorption, catalysis and cation exchange processes. Over the last several decades there has been particular focus on the capture of greenhouse gases using small-pore zeolites in response to the increase in the concentration of atmospheric carbon dioxide from anthropogenic sources [1]. Nanosized zeolites possesssignificantly high surface area and reduced diffusion path length for guest molecules compared to their micron-sized counterparts[2]. The use of organic structure-directing agents during synthesis to achieve specific zeolite topologies, compositions or particle morphologies is expensive due to the cost of the organic template which must be removed and destroyed by calcination after synthesis. Alternatively, inorganic cations can direct the formation of different zeolite topologies and morphologies while requiring fewer synthetic steps. Here we describe the synthesis oftwo nano-sized chabazite (CHA) zeolites using higher charge-density alkaline earth metal cations (Ba2+, Ca2+). The hydrothermal treatment was performed over different crystallization time to investigate the evolution of the nano-sized zeolites. The nano-sized CHA zeolites were comprehensively characterized by ICP-MS, SEM, XRD, DLS, TGA, N2 and CO2 physisorption, and 27Al and 29Si MAS NMR. As a reference material, nanosized CHA zeolite with crystals size of less than 200 nm and a Si/Al ratio of 2 was used. Microscopic and powder X-Ray diffraction analysis showed that the obtained CHA nanocrystals synthesised in the presence of barium crystallise faster under the same ageing and hydrothermal treatment conditions while retaining the same size and morphology. Thus, only four hours of hydrothermal treatment is needed to fully crystallize the nano-sized CHA in the presence of Ba2+ compared to 7 hours for the reference sample. Similarly, nano-sized CHA synthesised in the presence of Ca2+ crystallises less fast than in the presence of Ba2+ . Adsorption of CO2 on the nano-sized CHA samples was evaluated by in situ FTIR spectroscopic analysis. An equilibrium pressure of 0.77 kPa of CO2 under static conditions showed slower CO2 adsorption kinetics and lower uptake on the CHA sample prepared in the presence of Ba2+ than the reference CHA sample synthesised with Na+ , K+ and Cs+ only [3]. The adsorption-desorption cycling of CO2 at 6.6 kPa shows that the uptake is retained after three high vacuum regenerations at room temperature.

References

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