Advanced Characterisation and Operando Spectroscopies

FEZA21-OR-001

The location of defects in zeolites probed by solid state NMR

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Abstract Text: The distribution of silanols defects in zeolites has a major impact on their performance in industrial heterogeneous catalysis, adsorption, separation and advanced applications. The silanols defects in zeolites have major impact on the lifetime and selectivity of catalysts and sorbents that are the most probable deactivation sites[1]. Consequently, the location of silanols is of crucial importance but is still a difficult task because of the low resolution of diffraction techniques for low electronic density atoms like Hydrogen[2].

Solid-state Nuclear Magnetic Resonance (SSNMR) spectroscopy – offering unique structural and dynamical insights at the atomic scale – is a method of choice to localize silanols[3].

In this communication, we will present the latest results on the location of silanols defects in high siliceous zeolites using proton SSNMR. Characterized by the presence of strong dipolar homo-nuclear couplings, proton NMR gives precious information such as inter-nuclear distances. Then, by applying recoupling techniques, we were able to measure, with high precision, the distance between Hydrogen nuclei in silanols defects in nanosized MFI type zeolites synthesized with different organic structural directing agents and with variable particle sizes[4,5]. This opens new opportunities to modify zeolite properties by healing and/or creating silanol defects in zeolites for future applications.

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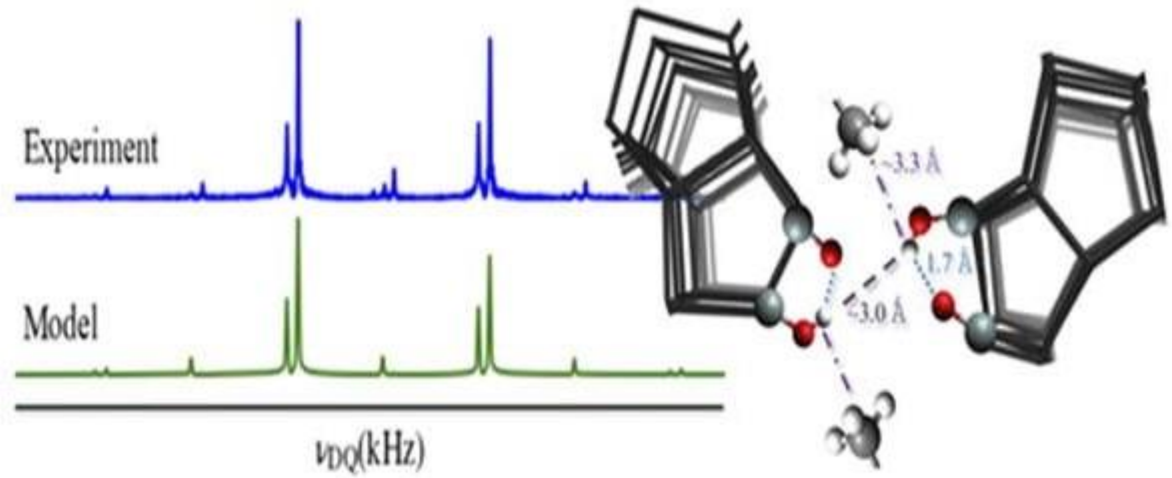
Image 1:



Advanced Characterisation and Operando Spectroscopies

FEZA21-OR-002

Nanoscale Visualization of Carbon and Magnesium Clusters in Zeolites Active in the Methanol-to-Olefins Process

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Abstract Text: In the methanol-to-hydrocarbons (MTH) process, methanol is converted to more valuable products, such as olefins and aromatics, using zeolite or zeotype catalysts. Methanol can be obtained from conventional as well as from more renewable sources, such as biomass, carbon containing waste and CO2, which explains the great commercial interest of this catalytic process. [1][2] The exact end-product of the process is determined by the zeolite pore structure and the number and nature of the acidic active sites. A key step in this MTH mechanism is the formation of a so-called hydrocarbon pool in which olefins and aromatic compounds function as activating and deactivating reaction intermediates. [3] Most of the unmodified proton form zeolites are extensively studied for their performance and deactivation in the MTH process. However, protons can be exchanged by other cations, which can drastically influence catalytic performance. [3] These influences on the catalytic behaviour are nonetheless not well understood.

In this work, magnesium was introduced in the chabazite structure SSZ-13. This resulted in differences in both catalytic performance as well as catalyst deactivation. Using *operando* UV-Vis spectroscopy and *operando* X-ray diffraction, differences between reaction intermediates and catalyst characteristics can be linked to the catalytic performance.

Zeolites are notoriously difficult to study at the nano-scale, because of their instability under e.g. electron beams. [4] Atom probe tomography (APT) is uniquely positioned among all tomographic techniques; it can provide 3D chemical information with sub-nm resolution, making it the only technique capable of finding nanometre scale relationships in these materials, and especially for studying elements that offer no significant z-contrast differences (e.g. Al and Si). With this technique we were able to visualize magnesium (Figure 1) and carbon clusters and obtain information about the distribution of these elements with respect to the aluminium (acid sites), as well as the correlation between magnesium and coke molecules after the MTH process.

To conclude, in this work both *operando* as well as APT studies on (un)-modified zeolites are described to be able to contribute to the unravelling of the MTH mechanism in the presence of e.g. Mg.

Image 1:

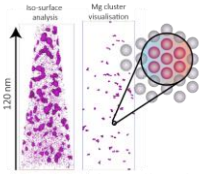

Figure 1: Visualization of magnesium rich areas and magnesium clusters

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Advanced Characterisation and Operando Spectroscopies

FEZA21-OR-003

Evidence of Hydronium Formation in Water−Chabazite Zeolite Using Inelastic Neutron Scattering Experiments and ab Initio Molecular Dynamics Simulations

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Abstract Text: A combined study of inelastic neutron scattering (INS) and ab initio molecular dynamics (AIMD) simulations has been performed in order to study the water−acid site interaction in zeolite chabazite with a ratio Si/Al = 16 that corresponds to 2 protons/uc with two different water coverages with the number of water molecules being lower and higher than that of proton sites. INS technique is mainly sensitive to vibrations involving hydrogen atoms because of their much higher incoherent cross section (σinc) compared to other elements. As a consequence, INS is well suited for investigating hydrated compounds, as water vibrations can be observed on a wide spectral range, even in regions where signals from the framework atoms would dominate the spectra in other vibrational techniques, for instance, IR or Raman spectroscopy. This allows us to overcome the interpretation of the complex spectra of IR spectroscopy and explore the low energy part that can give information about the H-bond network and that is strongly indicative of the coordination of the water molecule, i.e., the number of H-bonds formed. Another important feature is that the INS intensities are directly related to atomic displacements which can be computed from empirical force fields or from ab initio quantum chemical methods.

These results have provided a clear picture of the water−acid site interaction, and it has been demonstrated that at relatively high water loading (water/acid site ∼3), the clustering of water molecules and hydronioum cations formed by the complete transference of the zeolitic proton to the water molecules. The formation of water−hydronium clusters interacting with oxygen atoms of the zeolite framework provides the stabilization energy needed for the protonation of water molecules confined in the cavities of chabazite. The combined study of INS and AIMD simulations allowed us to identify the vibrational bands of hydronium cations and the water clusters [1]. These results are the experimental evidence obtained from INS of proton transfer from the zeolitic acid site and the hydronium formation and are in agreement with a previous computational study [2] and very recent solid state NMR spectroscopy studies [3]. The inspection of the low energy bands (translational and optic modes) and librational bands of the experimental results allows obtaining information about the H- bond network of the hydronium−water cluster. For instance, a signature of the presence of hydronium ions has been found in the increased intensity of the band at 1600−1700 cm−1 (antisymmetric bending mode), where the contribution near 1700 cm−1 is due to the hydronium ions as confirmed by ab-initio molecular dynamics.

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Advanced Characterisation and Operando Spectroscopies|Zeolites/Inorganic materials

FEZA21-OR-004

Fast Room-Temperature Lability of CHA Framework - 17O Solid-state Nuclear Magnetic Resonance Spectroscopy

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Abstract Text:

Zeolites are the most widely used inorganic supports in industry, with established applications in heterogenic catalytic and molecular sieve processes, ion exchange reactors and biomedical sectors.[1] A particular value of zeolites in industry is their tolerance to harsh operating conditions, particularly in processes when nucleophiles, such as water, are involved.[2] Zeolite frameworks, however, are known to exhibit lability under certain aqueous conditions; interzeolite conversions, such as post-synthetic transformation processes[3] and the ADOR (*Assembly, Disassembly, Organisation, Reassembly*) method[4] are well-known examples of how this lability in aqueous conditions can be exploited to form new and sometimes 'unfeasible' frameworks from pre-existing parent structures.

The lability of zeolite frameworks in interconversion processes results in changes to the long-range order of the material, often characterised by diffraction techniques.[5,6] Through the use of solid-state NMR spectroscopy, a technique sensitive to the local environment, we have observed that bond lability in zeolite frameworks in aqueous conditions is far more extensive than previously thought. Despite a zeolite framework being composed of approximately 2/3 oxygen, the nucleus is rarely studied using NMR spectroscopy, owing to the extremely low natural abundance (0.037%), moderate gyromagnetic ratio and quadrupolar (I= 5/2) spin of the only NMR-active isotope, ^{17}O. However, by simply exposing frameworks to isotopically-enriched $H_2{}^{17}O_{(l)}$at room temperature and pressure, we have observed facile ^{17}O enrichment of framework oxygen species on rapid timescales, without framework degradation. The interaction of ^{17}O-labelled water and zeolites can be tracked using *in-situ* high-resolution solid-state NMR spectroscopy and this has shown the exchange of ^{17}O into the framework in a range of silicate, aluminosilicate and germanosilicate frameworks.[7-9]

The experimentally observed bond lability for a protonated form of an industrially relevant chabazite (H^+-SSZ-13) has been predicted to proceed *via* a Grotthus-type mechanism, with energetic barriers to bond cleavage as low as ~30 kJmol^{-1}, enabled by the existence of a hydrogen-bonded network of water.[8] The present work explores and extends the general applicability of this mechanism, by investigating the effect that counteraction substitution and framework composition; silicon to aluminium ratio and heteroatom (B, Ti, Zn) content; has on the rate and extent of this surprising oxygen exchange within the **CHA** framework.

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Advanced Characterisation and Operando Spectroscopies|Zeolites/Inorganic materials

FEZA21-OR-005

Structural Analysis of Faulting in the Triclinic Zeolite UZM-55 and the new Polymorph: UZM-55FM

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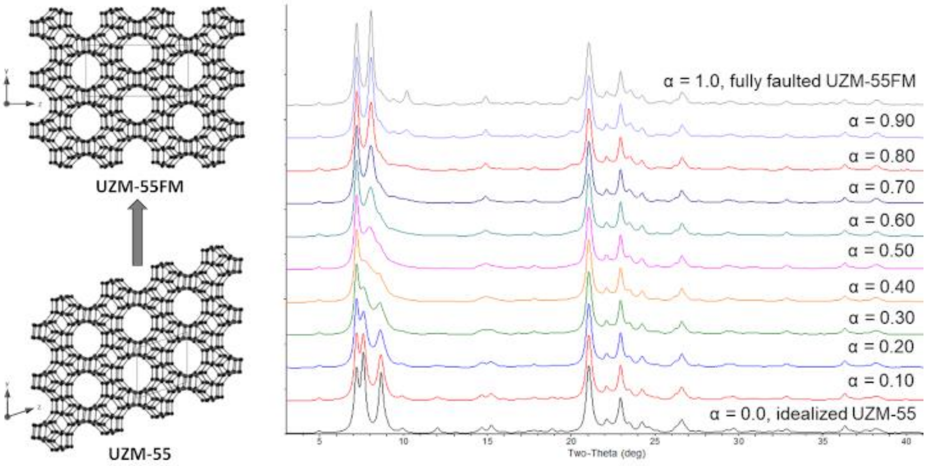
Abstract Text: Advances in acid-catalyzed catalytic reactions are often driven by new and modified zeolite structures. Topologies containing 10- and 12-membered ring pores are of particular interest as they create porosity in the size range appropriate for key industrial processes such as cracking and aromatics catalysis.[1] Recently, we reported the synthesis and idealized structure of UZM-55, which possesses a large triclinic unit cell and is one of the most structurally complex zeolites known. Related to MTW and MRE, both 10-MR and 12-MR delimiting rings are present in the kinked, one-dimensional pore, leading to interesting catalytic possibilities.

As the structure and connectivity present within a zeolite are a key defining feature leading to the observed performance, a complete structural description of the material is necessary to fully understand and predict the behavior of new zeolite materials. One notable hurdle to the structural analysis of zeolites is faulting. While not uncommon in zeolite and zeotype systems, faulting can create difficulty in fully characterizing materials, particularly in cases where the fully ordered end-members of the faulting have not been obtained in pure form. During preliminary structural work, it was noted that faulting was likely present in UZM-55 as observed via TEM imaging and diffraction work.

Here, the advanced characterization of the UZM-55 structure will be described leading to a model for the observed faulting and the generation of a new ordered end-member structure, UZM-55FM (for Faulted Model). Structural characterization data were used to propose a concept for the fault plane and together with model building a full tetrahedral-site connectivity model was generated of the perfectly faulted UZM-55FM polymorph. Both idealized UZM-55 and UZM-55FM contain the same kinked, one-dimensional pore containing 10-MR and 12-MR delimiting rings, but with different stacking sequences. Finally, to confirm the hypothesis, the DIFFaX program was used to model the faulted series and propose that experimentally synthesized UZM-55 possesses about 20% of this type of faulting which does not affect the pore undulation or delimiting 10-10-12-12-(10)-MR sequence.

Image 1:



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Advanced Characterisation and Operando Spectroscopies|Zeolites/Inorganic materials

FEZA21-OR-006

Dual-beam Fourier Transform Infrared Spectrometer: Applications and Potentials in Zeolite Catalysis

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Abstract Text: Introduction

FT-IR spectrometer is a powerful tool to collect the surface information of heterogeneous catalyst [1]. Until now, all the commercial FT-IR spectrometer is single-beam mode employing MCT or DTGS detector. During a typical FT-IR experiment, the background spectra should be collected before the sample spectra. Therefore, the time difference in-between background and sample spectra is inevitable in the commercial FT-IR spectrometer with single beam. The drawback of single-beam FT-IR spectrometer will be amplified when it is applied to collect surface information of heterogeneous catalyst under reaction conditions, e.g. heat irradiation and gas-phase molecular absorbance. In order to collect the background and sample spectra simultaneously, we designed a new dual-beam FT-IR spectral system (DB-FTIR) with two identical interferometer infrared optical platforms *via* the innovative strategy of coupling and integration. Tailor made dual-beam IR cell reactor could be used at wide range of temperature (-196 to 500℃) and pressures (-0.1 to 1.0 MPa). The dual-beam FT-IR spectral system and the dual-beam IR cell reactor together is suitable for the identification of weak absorbance between probe molecular and catalytic sites, and the study of the surface events occurred during various gas-solid phase catalytic reactions under reaction conditions. Furthermore, for the metal supported catalyst, the metal support interaction is crucial for catalytic performance. As the flexibility of choosing DB-FTIR background substrate, we could load support in the reference beam while metal-support catalyst in the sample beam. Thus, by the simultaneous deduction, we could decouple the interdependence between metal and support during reaction leading to better comprehension of the process.

Materials and Methods

The IR reactor cell was developed to have identical CaF2 windows to ensure total elimination of the background interference[2]. The effluent from IR reactor cell was analyzed by a quadrupole mass spectrometer (Omnistar, 1-200 amu, QMS 200). The CO adsorption was carried out at room temperature in continuous CO flow (6% CO, 94% N2, GHSV: $1080h^{-1}$) at the speed of 3 ml/min for 30 minutes.

Results and Discussion

To demonstrate the advantages of the DB-FTIR instrument as an operando spectrometer, an ordinary SB-FTIR spectrometer was compared with the DB-FTIR spectrometer by studying isobutene adsorptions on nano-sized HZSM-5 zeolite (SiO2/Al2O3 molar ratio = 26, crystal size = 20-50 nm), as shown in Figure 1(a). Spectra show that during the adsorption of isobutene, the DB-FTIR spectrum contained only four obvious absorption bands, which could be attributed to the species adsorbed on the surface of the zeolite. In contrast, when the ordinary SB-FTIR spectrometer was used, the obtained spectrum exhibited interference from gas-phase molecular vibration absorptions. This interference included not only weak absorptions in the region of 3072–3099 cm^{-1}, but also very strong absorptions in the region of 2800–3000 cm^{-1}; the latter strong absorptions were directly overlaid on the absorption bands of the surface species. The DB-FTIR could also collect the dynamic process of propene aromatization under reaction conditions (Figure 1(b) and (c)). Furthermore, DB-FTIR could identify the metal active sites over supported catalyst with weak interaction between CO probe (Figure 2).

Significance

The preliminary study shows that the performance of the most recently developed dual beam FT-IR spectral prototype system can satisfactorily overcome the shortcomings suffered by a single-beam FT-IR spectrometer. The dual-beam FT-IR system a powerful tool for the *operando* study of the surface dynamic chemistry of heterogeneous catalysis.

Image 1:

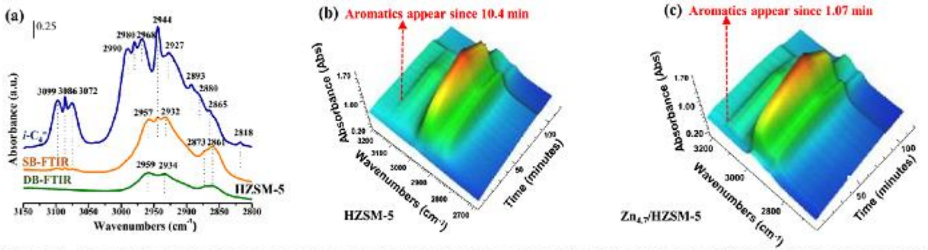

Figure 1. *Operando* study of isobutene and propene transformation over HZSM-5 and Zn modified HZSM-5 catalysts. (a) comparison of single beam FTIR (SB-FTIR) and dual beam FTIR (DB-FTIR) spectra of isobutene transformation (atmospheric pressure, 150°C, isobutene (6% $iC_4^=$, 94%N_2, GHSV: 1080h^{-1}; (b)-(c) propene transformation over DB-FTIR (atmospheric pressure, 250°C, $C_3^=$ (6% $C_3^=$, 94%N_2), GHSV: 1080h^{-1}).

Image 2:

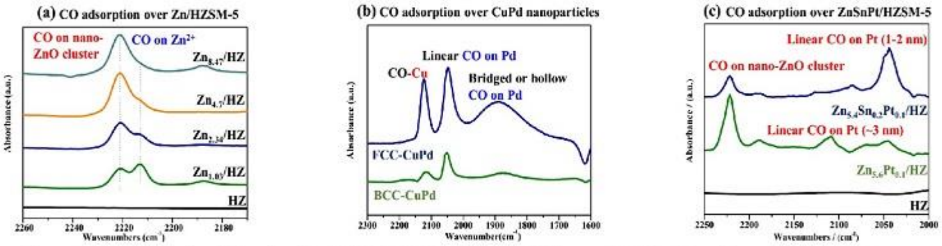

Figure 2. DB-FTIR study of CO adsorption (6%CO, 94%N_2, GHSV: 1080h^{-1}) over (a) HZSM-5 and Zn modified HZSM-5 catalysts, (b) CuPd@SiO_2 and (c) $Zn_xSn_yPt_z$/HZSM-5.

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Advanced Characterisation and Operando Spectroscopies|Zeolites/Inorganic materials

FEZA21-OR-007

Unravelling the structure of acid sites in trimethylphosphine oxide adsorbed HZSM-5 using 1H-31P HETCOR NMR

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Abstract Text: Probe molecules have been widely used to study the acid-base interactions with zeolites acid sites, providing information about acid properties namely acid site nature (Brønsted or Lewis), amount, accessibility and strength, which play a major role on predicting the overall catalytic activity of zeolites. Although the large amount of literature devoted to the characterization of acidity in solid acids, relevant questions regarding what is measured by probe molecules in acid zeolites are still under debate.[1]

Trimethylphosphine oxide (TMPO) has been suggested as an reliable and practical molecular probe to study the acidic properties of zeolites and other solid acid materials using solid-state NMR.[2] However, we have found that the interpretation of the one-dimensional (1D) ^{31}P NMR spectra of TMPO-loaded zeolites is quite inconsistent across the literature. Our work shows that two-dimensional (2D) ^{1}H–^{31}P heteronuclear correlation (HETCOR) NMR of TMPO-adsorbed zeolites, in tandem with DFT calculations, challenges previous assignments based on 1D ^{31}P NMR.[3] Data enabled an unambiguous discrimination of Brønsted and Lewis acid sites, and extended our understanding of TMPO:Brønsted complexes formed and the proton-transfer mechanism. We show that ^{31}P and ^{1}H chemical shifts of TMPO-loaded zeolites encode information beyond acid site strength and nature, providing information about the stabilization of neutral (TMPO···ZH) and charged ($TMPOH^{+}\cdots Z^{-}$ and $(TMPO)_2H^{+}\cdots Z^{-}$) ion pairs, whose geometry and amount depends on the pore structure/volume. The formation of higher-order complexes in TMPO-loaded zeolites raises questions regarding studies using TMPO and other probe molecules where similar complexes may form, which may lead to misinterpretation of NMR data.

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Advanced Characterisation and Operando Spectroscopies|Zeolites/Inorganic materials
FEZA21-OR-008

In-situ and ex-situ investigation of the Deca-Dodecasil 3 Rhombohedral zeolite for noble gas capture

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Abstract Text: Noble gas capture and purification have proven highly challenging. Xenon (Xe) is a precious and useful noble gas for semiconductor fabrication, lighting, aerospace, medical imaging, and anesthesia. Xe possesses a number of desirable properties as novel anesthetic gas such as favorable hemodynamics, lack of metabolism, and low solubility. Currently, Xe is merely produced as a by-product from cryogenic distillation of air. Because of the low abundance in the Earth's atmosphere (0.087 ppmv), intensive capital investment and energy consumption lead to an extremely high Xe price ($30,000–$60,000/m^3 gas, STP).

Recently, it has been shown that the Deca-Dodecasil 3 Rhombohedral (DD3R) zeolite exhibits a high selectivity, a good economic feasibility and long-term stability (>300 h) as membrane material for Xe production and recovery [1-3].

In this contribution, we have investigated the thermal behavior of the DD3R zeolite by in-situ powder diffraction and ex-situ single crystal diffraction from room temperature until 900°C. We show that upon initial heating and release of the trapped guest molecules, the zeolite undergoes a phase transition from R-3m to R-3 symmetries. The phase change is accompanied by the rotation of the silicate tetrahedra aligned along the c axis, allowing for a contraction of the cavities and an overall volume increase. Such situation is also observed for the completely activated DD3R, whose volume increase with respect to the as-synthesized conditions amounts to ~ 0.45% while the internal void is lower by ~ 0.8%. In addition, powder diffraction shows that the DDR zeolite exhibits a small negative thermal expansion of -5.6×10^{-6} in the initial removal of the guest molecules which drops to -3×10^{-6} upon heating the DDR zeolite without the guest molecules. We interpret this very small thermal expansion as the reason for the long-term stability of the zeolite. Finally, we show evidence for a lowering of the symmetry from rhombohedral to monoclinic at room temperature for the zeolite free from the guest molecules.

Figures 1 and 2 illustrates respectively the rotation mechanism and the in-situ thermal behavior of the DD3R zeolite upon heating and release of the guest molecules.

Image 1:

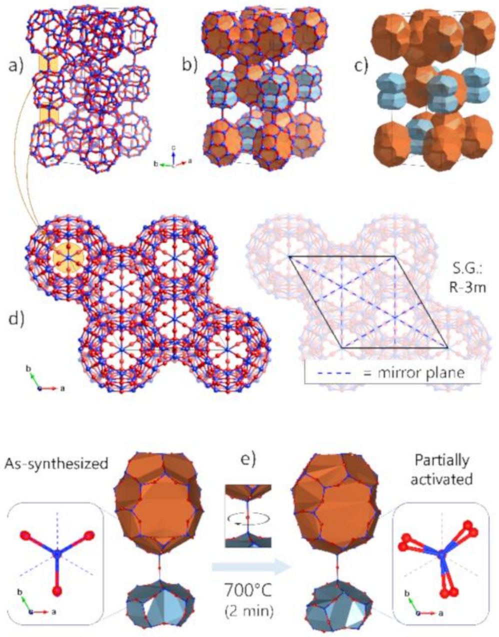
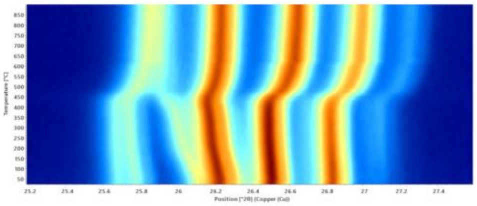


Image 2:



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Advanced Characterisation and Operando Spectroscopies|Zeolites/Inorganic materials

FEZA21-OR-009

Application of 3D electron diffraction techniques in developing novel zeolite materials

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Abstract Text: Zeolites are important crystalline microporous materials widely applied in catalysis, adsorption, and ion-exchange.[1] As the macroscopic properties of zeolites rely primarily on their microscopic structures, elucidating the fine structure information is essential for understanding zeolite materials and in turn facilitating their preparation and application. However, zeolites are typical powder materials with sub-micron-sized crystals and complex structures, which make their structure solution becomes difficult by single-crystal or powder X-ray diffraction. Compared with X-rays, electrons scatter much more strongly with the atoms in crystals, which allows obtaining the structure information of small single crystallites. Especially, the recently developed 3-dimentional electron diffraction (3D ED) techniques provide more opportunities for phase analysis and structure determination of zeolites that often occur as nanocrystals or multiple phases.[2,3]

Herein, we introduce new opportunities for novel zeolite materials discovery with the 3D ED techniques. SCM-15 (**SOV**) is a new zeolite containing a 3D channel system with interconnected 12×12×10-ring channels.[4] Its complete framework structure was identified directly with the direct method (*SHELXS*) based on the 3D ED data, together with traces of organic structure-directing agents (OSDAs), F^- ions, and framework Ge locations (Figure 1). The results were further verified with Rietveld refinement against the powder X-ray diffraction data. The fine structure information elucidated by 3D ED techniques is crucial for understanding guest-host interactions and rationally synthesis of zeolite materials. Another example is the new zeolite ECNU-23 unravelled from the "pure" powder sample of ECNU-21 with the 3D ED technique.[5] A crystal (ECNU-23) with different unit cell and framework structure was detected in the "pure" sample of ECNU-21 (Scheme 1). Based on the revealed framework structure, the synthesis was modified to successfully isolate a pure product of ECNU-23. The recent outcomes demonstrate the power of the 3D ED techniques for identifying minor phases in a mixture product to facilitate the preparation of target zeolite materials.

Image 1:

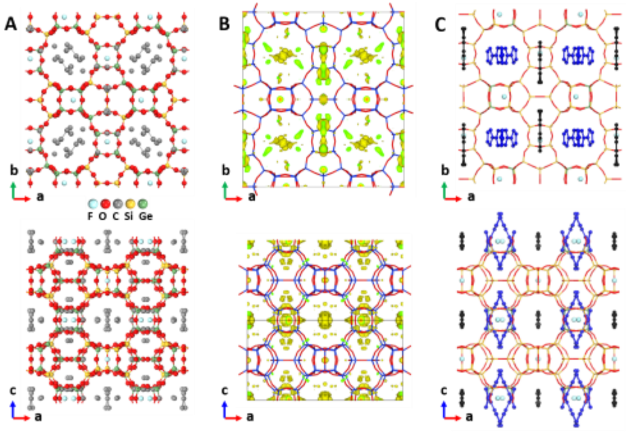
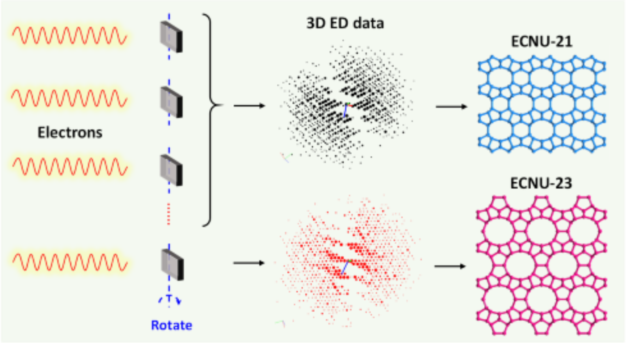


Figure 1 Structure details of SCM-15. A) Initial structure model resolved by direct method (SHELXS) based on 3D ED data. B) Residual electron density map generated based on PXRD data. C) Refined structure based on PXRD.

Image 2:



Scheme 1 3D ED unravels the new zeolite ECNU-23 from the "pure" powder sample of ECNU-21

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Advanced Characterisation and Operando Spectroscopies|Zeolites/Inorganic materials

FEZA21-OR-011

Structure and reactivity of mobilized Cu-oxygen pairs and their role in the low temperature NH3-Selective Catalytic Reduction

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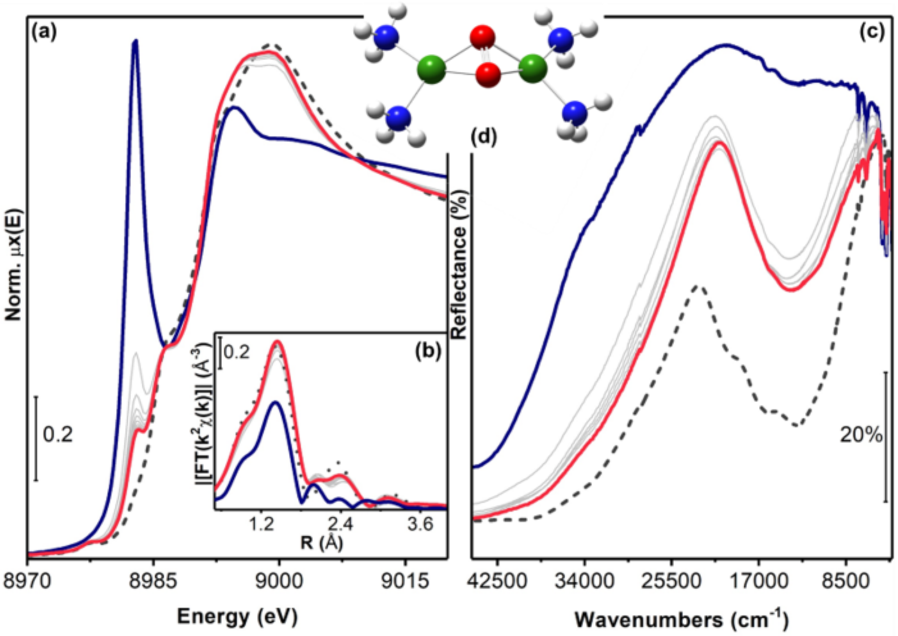
Abstract Text: The Selective Catalytic Reduction with ammonia (NH_3-SCR) reaction is the state-of-the-art technology to abate NO_x emissions from lean burn heavy-duty and passenger car vehicles. Currently, Cu-exchanged chabazite zeolites (Cu-CHA) are the catalysts of choice, with a good performance over a wide range of temperatures.[1] Notwithstanding many in-depth studies about Cu speciation and reaction intermediates, some aspects of the NH_3-SCR mechanism over Cu-CHA are still debated.[2-6] A crucial step of the reaction is the (slow) oxidation half-cycle, where O_2 needs to be activated by Cu^I to re-establish the Cu^{II} active site able to release N_2 and H_2O as products.[3] O_2 activation has been proposed to be mediated by NO at high temperature or, in the low temperature regime (<250 °C), to involve solvated $Cu^I(NH_3)_2$ pairs with the formation of $[Cu_2(NH_3)_4O_2]^{2+}$ mobile complexes.[4, 6] To the best of our knowledge, the structure of these proposed intermediate complexes is still not known. Therefore, in this contribution we present the results obtained applying *operando* X ray absorption (XAS) and Diffuse Reflectance (DR) UV-Vis spectroscopies, supported by DFT optimized structures for EXAFS fitting and Wavelet Transform Analysis (WTA), to study the nature of the proposed $[Cu_2(NH_3)_4O_2]^{2+}$ mobile complex in a Cu-CHA sample with Si/Al=15 and Cu/Al=0.5 (Cu density ~ 0.45 Cu/1000 $Å^3$). Finally, the reactivity of $[Cu_2(NH_3)_4O_2]^{2+}$ complexes will be discussed.

Figure 1 reports the XAS and DR UV-Vis spectra of the $[Cu_2(NH_3)_4O_2]^{2+}$ complexes formed by reacting mobile $Cu^I(NH_3)_2$ moieties (blue curve) with O_2 at 200 °C (light grey to red curves). The Cu^I/Cu^{II} re-oxidation results in ~ 85% of oxidized copper, in good agreement with theoretical predictions [3]. The final Cu^{II} state can be clearly distinguished from the Cu^{II} state obtained after by direct O_2 oxidation (red *vs* dark grey spectra). The experimental EXAFS spectra were successfully fitted with a DFT computed peroxo-side on structure (Figure 1d). The presence of Cu-Cu dimers was further proven by WTA, allowing the discrimination of second shell scattering contributions around the absorber. The reaction of the proposed $[Cu_2(NH_3)_4O_2]^{2+}$ mobile entities with NO or NH_3 alone resulted in different mixtures of Cu^{II}/Cu^I species, showing that O_2 dissociation does not occur in the presence in ammonia, but necessarily requires NO. These finding points to the fact that the $[Cu_2(NH_3)_4O_2]^{2+}$ complex is rather inert with respect to ammonia, while is capable to activate NO, which then results in the SCR activity.

<u>Figure 1</u>: *Operando* (a) XANES, (b) EXAFS and (c) UV-Vis DR spectra of Cu-CHA exposed to O_2/He at 200 °C (light grey to red curves) after reduction in NO/NH_3/He at 50 °C (blue curve). Dark grey dotted curve: O_2-activated Cu-CHA. (d) $[Cu_2(NH_3)_4O_2]^{2+}$ peroxo side-on complex, Cu, green; H, white; O, red; N, blue.

Image 1:



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Advanced Characterisation and Operando Spectroscopies|Zeolites/Inorganic materials

FEZA21-OR-012

Confined species shaping the lifetime of zeolite catalysts for methanol conversion

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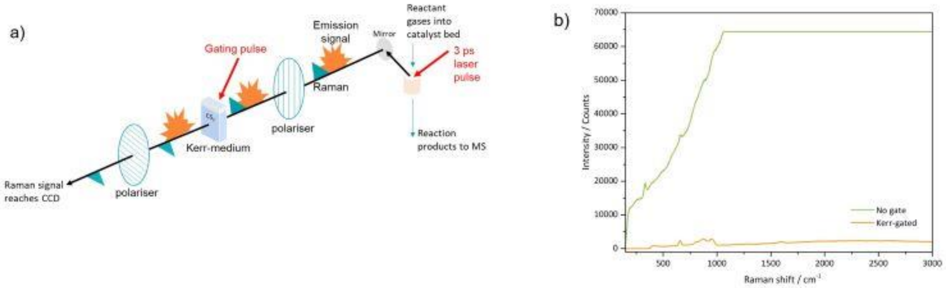
Abstract Text: Sustainable chemical production of light olefins from coal, natural gas or biomass can be realized at a large scale through a multi-step process involving methanol synthesis from syngas followed by methanol conversion on zeolite catalysts (methanol-to-hydrocarbons, MTH). Depending on the reaction conditions and zeolite topology used, product selectivity can be adjusted towards light olefins, aromatics or gasoline, allowing circumventing current oil-based technologies such as naphtha cracking.[1] Process efficiency and catalyst stability are however, strongly compromised by the formation of carbon deposits during operation,[1] so a better understanding of the mechanism of catalyst operation and eventual deactivation is required for improved catalyst design.

Raman spectroscopy using a visible excitation source is a powerful technique for studying the evolution of carbon species under reaction conditions, but its application to zeolite catalysts is often limited by strong sample fluorescence that swaps the Raman signal. This can be circumvented by using an alternative excitation wavelength however, while near infrared radiation leads to weak Raman scattering, ultraviolet excitation is more likely to cause photodegradation. In this work, operando Raman measurements using a visible excitation source have been performed in combination with a Kerr-Gated spectrometer - which distinguishes a Raman signal from background fluorescence based on their differing lifetimes (see Figure 1).[2] This unique approach has provided compelling evidence into both active and deactivating species formed on both SSZ-13 and ZSM-5 during methanol conversion- typically overshadowed by emission when no gating is applied, and their connection with the various stages of the MTH process.[3]

Image 1:



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Advanced Characterisation and Operando Spectroscopies|Zeolites/Inorganic materials

FEZA21-OR-013

Zeolites Heterogeneous Catalysts Caught in the Act by (Dynamic Nuclear Polarisation) Magic Angle Spinning NMR

F. Blanc*

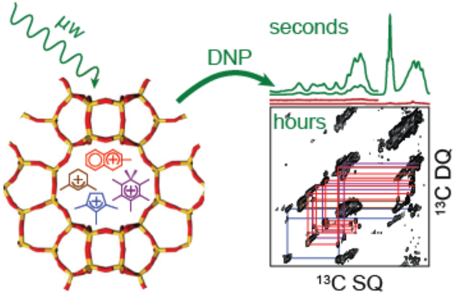
Abstract Text: The formation of carbocation intermediates plays a key role in reactivity, selectivity and deactivation in heterogeneous catalytic processes. However, their observation and determination remain a significant challenge due to the lack of selective techniques of sufficient sensitivity to detect their low concentrations (< 10 mmol/g).[1,2] We will show how an approach combining ^{13}C isotopic enrichment with multinuclear NMR and, on selected occasions, efficient Dynamic Nuclear Polarisation (DNP) Magic Angle Spinning (MAS) NMR at 9.4-14.1 T using bisnitroxide radicals as polarising agents, allows the fast detection of carbocations formed during catalysis. The approach is demonstrated in a range of zeolites with different topologies including in Mobil-type five (MFI, *e.g.*H-ZSM5),[3] Zeolite beta polymorph A (BEA, e.g. beta zeolite)[4] and chabazite (CHA, *e.g.*H-SSZ-13, H-SAPO-34).[5]

We use two dimensional ^{13}C-^{13}C through-bond correlations (Figure) to establish the carbon-carbon connectivity and unambiguously derive 5- and 6-membered ring cyclic carbocation and methylnaphthalenium ions as intermediates in the methanol to hydrocarbons catalytic reaction. We also showed that these species could be different even in zeolites with identical CHA topology.[5] These highlight that different catalytic routes exist for the formation of both targeted hydrocarbon products and coke exist..

We employ both ^{29}Si-^{13}C and ^{27}Al-^{13}C through-space experiments to quantitatively locate the confined carbocations with respect to the multiple surface sites of the zeolites, demonstrating that these species have strong van der Waals interaction with the frameworks and that their accumulation in the channels leads to deactivation. These results, obtained from multidimensional multinuclear (DNP) MAS NMR, enable understanding of deactivation pathways and open up opportunities for the design of catalysts with improved performances.

We also show that introducing hierarchical pores into zeolites to form micro-meso-macroporous zeolite frameworks is a promising way to dramatically improve the overall DNP efficiency by a factor of ~ 4 on this type of materials[4] and may be a general method that could be applicable to other porous solids.

Image 1:



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Advanced Characterisation and Operando Spectroscopies|Zeolites/Inorganic materials
FEZA21-OR-014

The role of water during zeolite formation in hydrated silicate ionic liquids

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Abstract Text:

The success of zeolite technology for industrial applications in catalysis, adsorption, and ion exchange has driven research to understand and control the mechanism of zeolite formation. While these efforts led to numerous zeolite formation models, many questions remain unanswered[1]. Recent studies demonstrate the advantages of rational science over exploratory studies to unravel this formation mechanism, although these efforts depend on the use of organic templates and are mostly limited to reverse-engineering. Scientific breakthroughs are not forthcoming as the presence (non-)equilibrium gel(-like) phases and a lacking characterization toolbox do not allow quantitative interpretation of the crucial solution-mediated chemistry[1].

Recently, a new zeolite formation strategy based on hydrated silicate ionic liquids (HSILs) was reported[3]. This approach exploits spontaneous phase separation during hydrolysis of tetraethoxysilane in alkali hydroxide solutions, resulting in optically transparent and homogeneous silicate ionic liquids. Doping such HSILs with controlled aluminate sources leads, upon heating, to the controlled formation of numerous zeolite topologies (ABW, ANA, CHA, CAN, EDI, FAU, GIS, JBW, MER, LTL, PHI, SOD). This synthesis approach starts from an optically transparent, colloid-free solution that enables the study of solution-mediation in the absence of a gel phase. Due to the close compositional relationship between HSIL and traditional zeolite synthesis, a full and general understanding of hydrothermal zeolite formation is within reach.

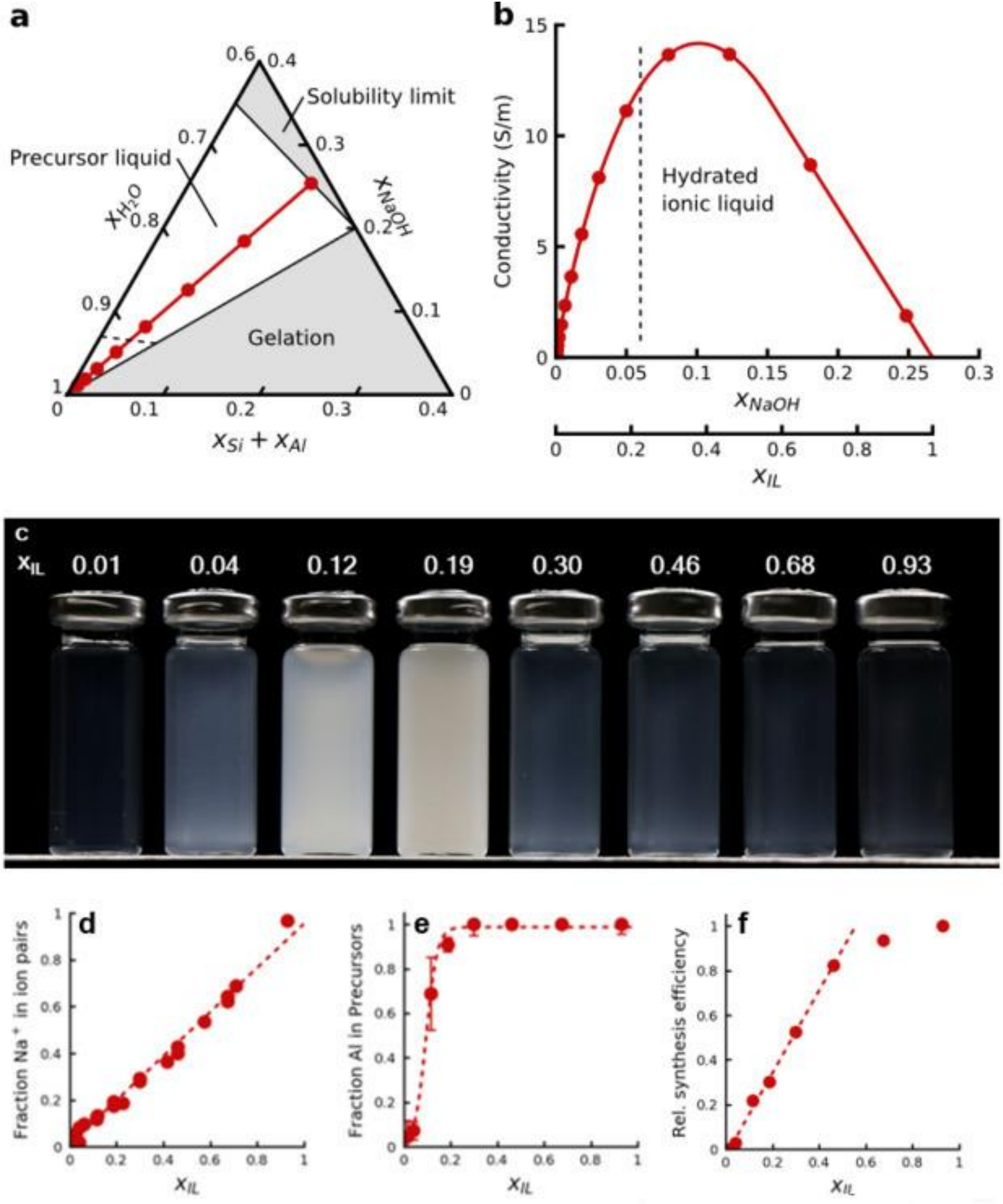
We report the novel application of a characterization toolbox that allows quantitative insights into the chemistry of room-temperature HSIL zeolite precursor liquids. On the one hand, we designed a device for advanced conductivity measurements that allow determining the ionic state of a liquid with an average accuracy of 0.23%[4]. Combined with ^{1}H, ^{23}Na, ^{27}Al, ^{29}Si liquid-state MAS NMR, this toolbox enables a true and quantitative description of water chemistry, the prevalence of ion pairs, and the incorporation of T-atoms in zeolite precursors.

In this abstract, we employ this toolbox to elucidate the role of water in alkaline aluminosilicate zeolite formation. For this purpose, the water content was varied in zeolite precursor liquids of composition 0.5 $Si(OH)_4$: 0.025 $Al(OH)_3$: 1 NaOH : n H_2O, with $2.5 < n < 350$ (Fig. 1a), the room-temperature chemistry was quantitatively described, and the synthesis outcome and efficiency were evaluated via high-resolution x-ray diffraction. With decreasing water content, a conductivity drop is observed despite the nominal charge density increase (Fig. 1b, x_{NaOH} and x_{IL} refer to molar fractions of NaOH and ionic liquid). Such behaviour implies ion-association, where the presence of free charges is significantly reduced via ion pair formation[5]. When water is a limiting reagent, sodium cations are unable to coordinate a full hydration shell and, in the absence of other options, rely on non-water species to complete the hydration complex. As a result, a hydrated ionic liquid forms, transforming the liquid from an opaque colloidal solution to a transparent true liquid (Fig. 1c).

We confirm that ion-pairing proceeds between sodium cations and aluminosilicate oligomers[6], ensuring full conversion of T-atom sources into zeolite precursors (Fig. 1d-e). We prove that both the (in)stability of precursors and ion pairs is detrimental to achieve efficient zeolite formation (Fig. 1f). By rational optimization of the water content, we synthesize phase pure zeolites at mild conditions (60°C, 168h), while increasing the synthesis efficiency twentyfold, approaching

total conversion in the concentrated case. Furthermore, ion-pairing should facilitate on-demand design and condensation of zeolite precursors. Zeolite synthesis in hydrated silicate ionic liquids features satisfactory properties to study solution-mediated processes in the early zeolite formation.

Image 1:



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Catalytic Properties

FEZA21-OR-015

Metalloenzymes vs. Metallozeolites: Exploiting the Similarities and the Differences

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Abstract Text: The similarities between enzyme catalysis and zeilte catalysis have drawn interest from the research community since decades. The observation of confinement effects on selectivity in acid catalysed reactions was a first example. Enzymes have later on inspired the design of zeozymes with encapsulated metal organic complexes. The latter have however, never really taken off. Both zeolites and enzymes have desirable but also undesirable properties for industrial catalysis. Ideally, the catalyst lends its stability from the zeolite, and combines this with enzyme-like concepts that can be designed into the zeolite. In recent work (some of which is still under review at the time of writing this abstract) we have shown experimentally that several new enzymatic concepts translate to zeolites.

A first concept is the entatic state, where a rigid matrix imosed a rective state on an intermediate and reduces the activation barrier. In enzymes this rigid matrix is would be the protein mantle. While entatic states in enymes remain debated, we have for the first time and unambiguously demonstrated their role for the N2O ativation on the alphaFe active site and for the H-atom abstraction by the alphaO active site in Fe zeolites.

A second concept is the cage effect that in enzymes controls recombination of reactive intermediates versus their reaction with distant reactive centres on the catalyst. While broadly classified as a confinement effect, this cage effect had never been demonstrated experimentally in zeolites, while it has convincingly been evidenced on enymes and some encapsulated homogeneous catalysts.

Thirdly we note that the zeolite environment enables a surprising diversity of coordination environments for transition metal centres, even without the help of flexible organic ligands as used in the zeozymes. Aluminium distribution and topology choice play an important role and allow for rational design. Even the small differences in geometry that are accomodates by different zeolites give rise to spectacular differences in spectroscopy, reactivity and selectivity. We show this for catalysis with Fe and Cu exchanged zeolites.

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Catalytic Properties

FEZA21-OR-016

Impact of extra-framework clusters in zeolites on alkane cracking

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Abstract Text:

Introduction

Catalytic active sites in zeolites are constituted by both the bridging SiOHAl groups that act as Brønsted acid sites (BAS) and by surrounding microporous cavities that solvate confined species involved in catalytic cycles [1]. Both the cavity framework and extra-framework species afford such constraint and solvation and influence catalytic reactions [2]. The presence of extra-framework alumina (EFAl) in proximity of a BAS enhances its catalytic activity in n-pentane cracking by 50 folds. Extra-framework silica (EFSi) is another type of extra-lattice species, however its role in catalytic reactions is hitherto unidentified. Here we controllably create EFSi in the vicinity of BAS ion MFI zeolite, and show the different mechanisms for the enhancement of catalytic activity in protolytic cracking of n-pentane in comparison to that of EFAl.

Materials and methods

Parent H-MFI zeolite was obtained by dealuminating on a commercial H-MFI (CBV 2314 from *Zeolist*) with ammonia hexafluorosilicate and further calcination at 773K. EFAl was created by controllable steaming of the parent H-MFI. EFSi was grafted into H-MFI by adsorbing n,n-dimethyltrimethylsilylamine and calcined at 773K for 5h.

The concentration of acid sites was analysed by IR spectroscopy of adsorbed pyridine. Adsorption of pentane was studied by means of IR spectroscopy under different partial pressure. The protolytic cracking of n-pentane was investigated in a fixed-bed reactor.

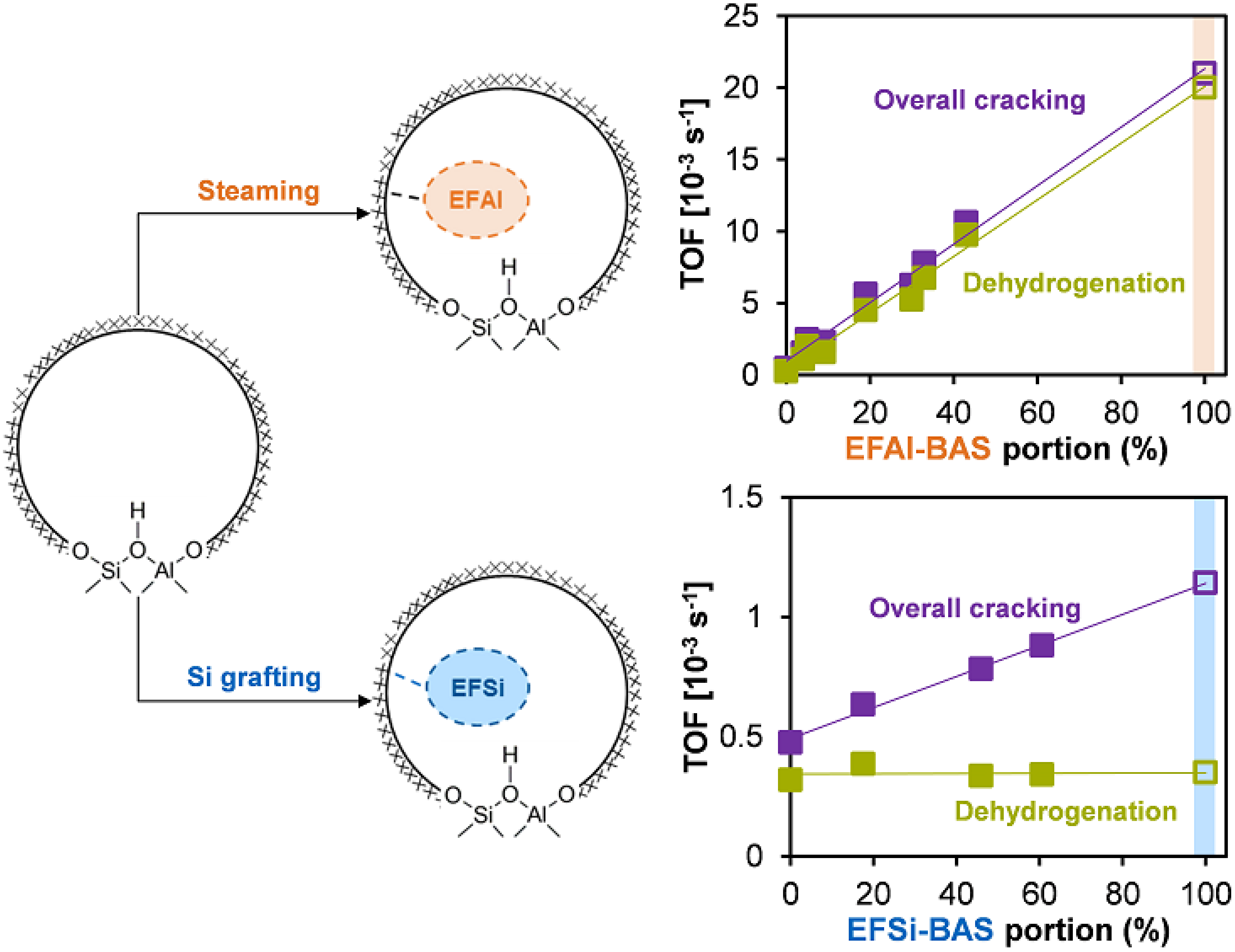
Results and discussion

The presence of EFAl or EFSi in H-MFI makes a portion of BAS with nearby EFAl or EFSi. In order to differ from normal BAS, they are denoted as EFAl-BAS or EFSi-BAS. The turnover frequencies (TOFs, rate normalized to total BAS) for overall cracking, dehydrogenation and different cracking pathways of n-pentane reaction on MFI zeolites all show linear increase with the portion of EFAl-BAS or EFSi-BAS in the total BAS (Figure 1). By extraploting TOFs to 100%, the TOF of all reaction pathways were obtained for EFAl-BAS and EFSi-BAS. As shown in Figure 2, the TOF on EFAl-BAS is 50-fold higher than normal BAS. This significant of enhancement was attributed to the higher transition entropy, overcompensating the increase of the activation energy. However, on EFSi-BAS, the increment of TOF was only 2-fold higher. This enhancement was attributed to the lower activation energy.

Conclusion

Both extra-framework species in zeolite, i.e., EFAl and EFSi, enhance the catalytic activity of BAS in alkane cracking. However, the EFAl promotes the reaction via increasing the transition entropy, while EFSi via decreasing the activation energy, indicating different mechanisms for the rate enhancement.

Image 1:


Steaming
EFAl
Si grafting
EFSi
H
O
Si
Al
O
O
TOF [10^{-3} s^{-1}]
25
20
15
10
5
0
0
20
40
60
80
100
Overall cracking
Dehydrogenation
EFAl-BAS portion (%)
TOF [10^{-3} s^{-1}]
1.5
1
0.5
0
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20
40
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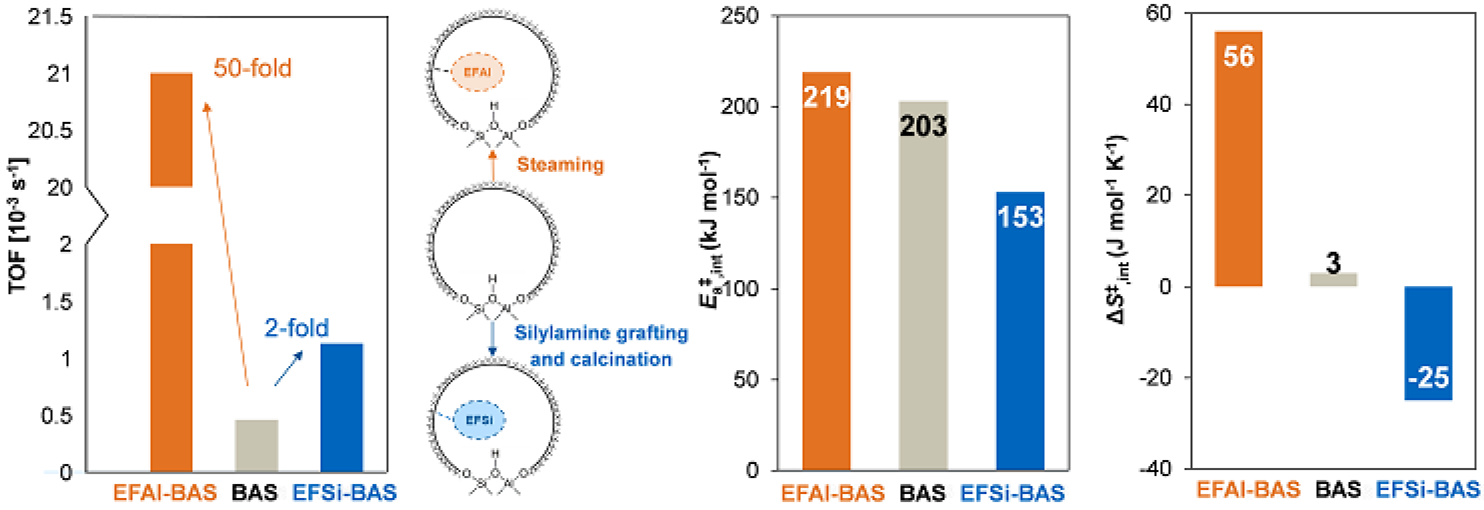
80
100
Overall cracking
Dehydrogenation
EFSi-BAS portion (%)

Image 2:



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Catalytic Properties

FEZA21-OR-017

Hollow Titanosilicate Nanospheres Encapsulating PdAu Nanoparticles for H2O2-mediated One-pot Oxidation Reaction

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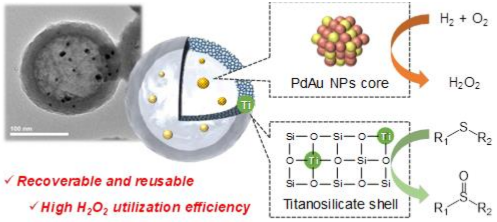
Abstract Text: A tandem reaction combining direct H_2O_2 production from H_2 and O_2 and subsequent oxidation reaction with H_2O_2 in a single reaction vessel offers an energy-saving and cost-effective oxidation route for the synthesis of targeted chemicals. In primitive studies, Pd NPs loaded on titanosilicate supports (TS-1, Ti-MCM-41) with high surface areas and defined porous structures were used to pursue the high dispersion of Pd NPs and thus to create highly exposed active sites for H_2O_2 production. However, uncontrolled size of Pd NPs, growth of the particle size during the reaction, and limited accessibility of reactants to Ti site resulted in poor catalytic activities. In order to improve the catalytic efficiency in the one-pot oxidation reaction, alternative titanosilicate supports possessing different nanostructures, such as core-shell-type titanosilicate catalyst, was recently developed [1-2].

In this study, we report the synthesis of hollow titanosilicate nanospheres encapsulating Pd and PdAu alloy nanoparticles (NPs) for the H_2O_2-mediated one-pot oxidation reaction [3-4]. The yolk–shell nanostructured catalysts (Pd@Ti-HMSS), composed of Pd NPs core encapsulated within a hollow mesoporous titanosilicate shell having isolated Ti atoms, are fabricated by a facile etching and re-assembly process using SiO_2 spheres as a template and two different kinds of Si alkoxide as precursors. The synthesized catalyst shows superior catalytic activity in the one-pot oxidation reaction of sulfide under a co-flow of H_2 and O_2, which far outperforms those of the prototype titanosilicate-supported Pd NP catalysts. Detailed structural characterizations and kinetic analysis unravel that the increased catalytic efficiency is attributed to efficient mass transfer of reactants and the associated improved reactivity with in-situ generated H_2O_2 over Ti sites. A further enhanced activity is achievable by encapsulating PdAu alloy NPs, which provide a faster H_2O_2 production rate than monometallic Pd NPs. Owing to the presence of protective silicate shell, the catalyst shows a good stability and reusability over multiple catalytic cycles without significant loss of activity.

Image 1:



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Catalytic Properties

FEZA21-OR-018

Diffusion of [Cu(NH3)2]+ complexes in Cu-CHA catalysts under NH3-SCR-NOx reaction conditions: insights from AIMD simulations

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Abstract Text: One of the most successful technologies to cope with nitrogen oxides (NO_x) emissions from stationary power plants and diesel vehicles is the selective catalytic reduction (SCR) in which ammonia is used as reducing agent (NH_3-SCR-NOx) [1-3]. The catalysts currently employed in transport applications are copper–exchanged zeolites, in particular those possessing small-pore structures such as the CHA [4-7].

Operando X-ray absorption and emission (XAS/XES) spectroscopic studies have shown that at low temperature (T < 473 K) ammonia liberates the Cu^+ ions from its coordination with the zeolite framework forming mobile $[Cu(NH_3)_2]^+$ species. These mobile amino-copper complexes are responsible for the activation of O_2 through the formation of the transient dimeric species $Cu(NH_3)_2$-O_2-$Cu(NH_3)_2$ [8-10]. The diffusion of the monomeric $[Cu(NH_3)_2]^+$ species to the adjacent cavity through the 8r window is the rate-determining step at low Cu loading. At higher temperature (T > 523 K), the Cu^+ and Cu^{2+} cations occupy their framework positions in the 6-ring or 8-ring windows of the zeolite structure, forming a true heterogeneous single-site catalyst.

In this work, we apply AIMD simulations and enhanced umbrella sampling (US) techniques to obtain Gibbs free energy profiles for the diffusion of $[Cu(NH_3)_2]^+$ complexes through the 8-ring windows of SSZ-13 zeolite (Image 1) in the presence of other reactant molecules, namely NO, O_2, H_2O and $NH_{3,}$ at a temperature of 423 K representative of the low temperature regime.

The calculated Gibbs free energy of activation for the diffusion of an isolated $[Cu(NH_3)_2]^+$ complex through the 8-ring windows of the chabazite structure is relatively low (~17 kJ/mol), showing that this process is fast (blue line in Image 2). Moreover, the free energy profile is not significantly modified when another $[Cu(NH_3)_2]^+$ monomer, NO or O_2 molecules are in the final cavity B. In contrast, the diffusion of is $[Cu(NH_3)_2]^+$ significantly hindered when reactant molecules, in particular NH_3 and NO, are present in the initial cavity A. NH_3 forms hydrogen bonds with the ligands of the complex and with the framework O atoms, while NO binds to the central Cu^+ atom forming relatively stable $[Cu(NH_3)_2(NO)_2]^+$. In both cases, the stable intermediates formed are too bulky to cross the 8-ring window, and the necessary de-coordination of the additional ligands involves an energy penalty reflected in higher activation and reaction free energies (orange and green lines in Image 2). Therefore, the local concentration of some particular reactants in the vicinity of the copper active sites is identified as a key factor strongly influencing the mobility of $[Cu(NH_3)_2]^+$ species at low temperature.

On the other hand, the presence of O_2 in the reaction media weakens the interaction of NO with Cu^+, detaching it from the stable $[Cu(NH_3)_2(NO)_2]^+$ complex formed under reducing conditions. This facilitates the migration of the resulting $[Cu(NH_3)_2]^+$ species through the 8-ring windows of the CHA to form the dimers involved in the oxidation step. Furthermore, at high temperature (673 K), O_2 reacts with the two NO molecules present in the cavity to form two NO_2 molecules, with an activation free energy barrier of only 25 kJ/mol and without the direct participation of the Cu^+ cation in the reaction. These results confirm the existence of two different reaction mechanisms operating at low and high temperatures, the former involving dimeric $Cu(NH_3)_2$-O_2-$Cu(NH_3)_2$ species and the later occurring by direct NO oxidation to NO_2 in one single cavity.

Image 1:

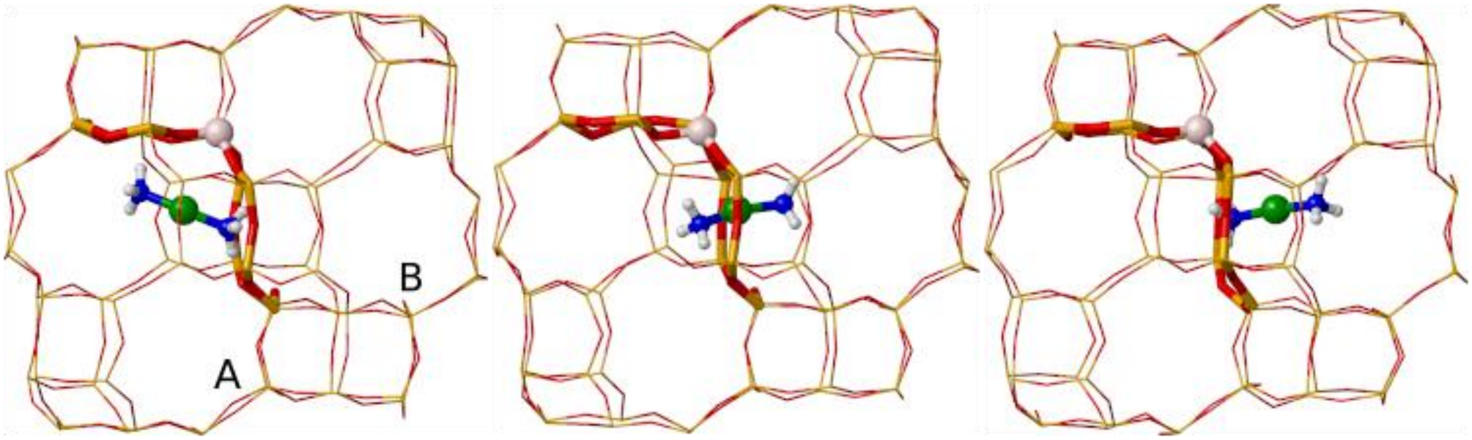
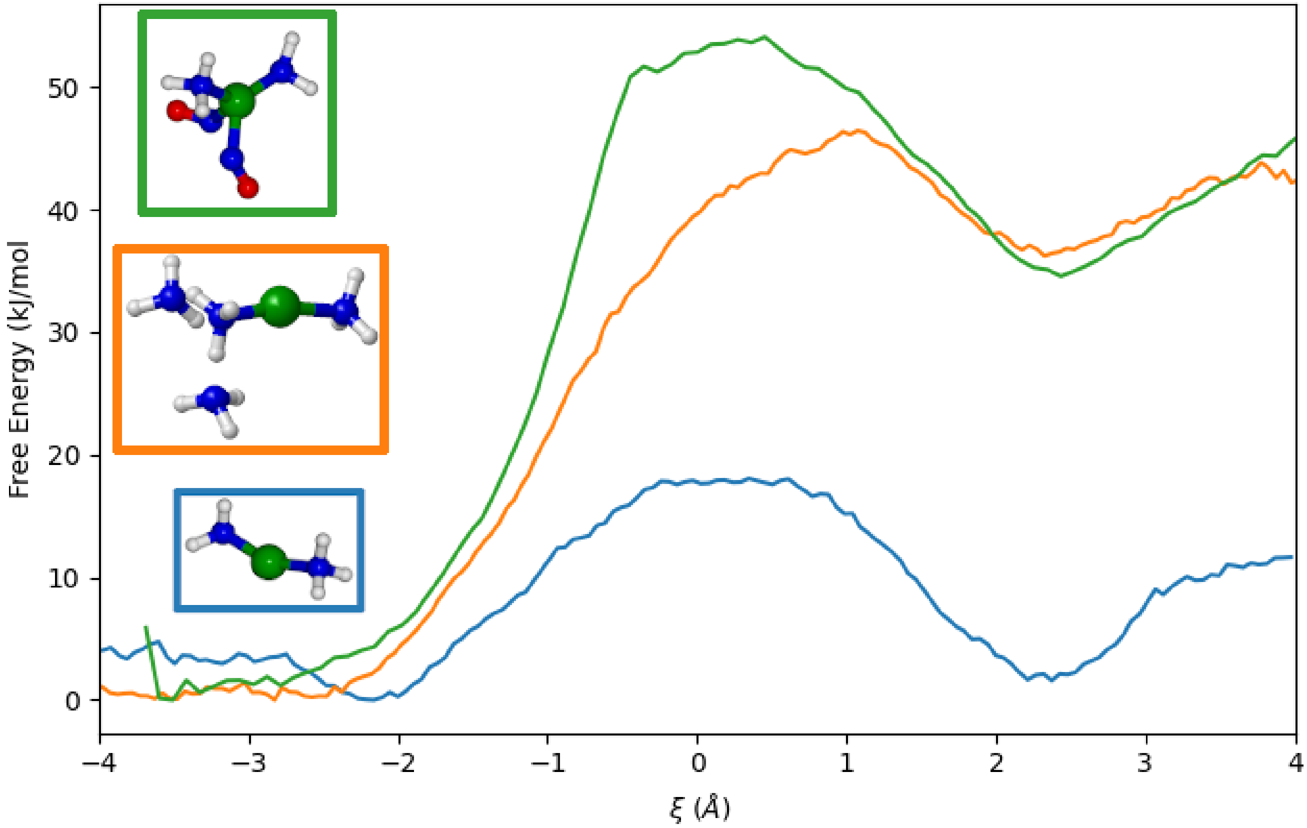


Image 2:



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Catalytic Properties

FEZA21-OR-019

Understanding the Correlation between Ga Speciation and Propane Dehydrogenation Activity on Ga/H-ZSM-5 Catalysts

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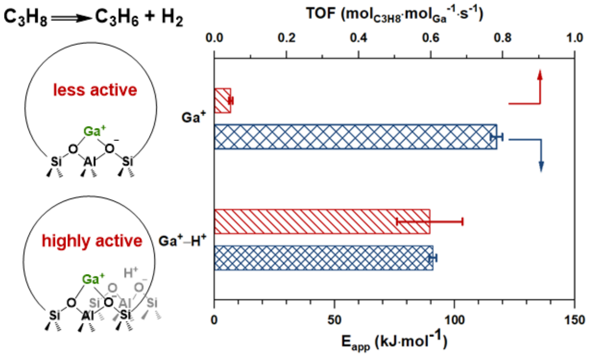
Abstract Text: H-ZSM-5 zeolite supported Ga (Ga/H-ZSM-5) has been recognized as a selective catalyst for non-oxidative propane dehydrogenation (PDH) for decades, however, the reaction mechanism remains a topic of considerable discussion. In particular, the correlation between various Ga species present on the catalyst at the reaction conditions and the PDH activity has yet to be established. In this work, intrinsic PDH rates and activation energies were determined on Ga^+−H^+ pair sites and isolated Ga^+ sites for the first time on Ga/H-ZSM-5 samples with a wide range of Si/Al and Ga/Al ratios. The turnover frequency on Ga^+−H^+ pair sites in the PDH is higher than that of isolated Ga^+ by a factor of ~15. Experimental measurements combined with a dual-site model show the activation energy in the PDH on the Ga^+−H^+ pair sites and isolated Ga^+ sites to be 90.8 ±1.5 and 117 ± 4.7 $kJ\cdot mol^{-1}$, respectively. These results demonstrate that Ga^+−H^+ pair sites are much more active in the PDH than isolated Ga^+ sites. Activation energy of GaH_x decomposition to form H_2 was determined to be 40-60 $kJ\cdot mol^{-1}$ higher than that of the PDH on Ga species, suggesting that the GaH_x decomposition is unlikely to be part of the PDH mechanism. Although both Brønsted acid and Ga sites interact with propane, FTIR results provide strong evidence suggesting that the alkyl mechanism is more likely in the PDH on Ga/H-ZSM-5.

Image 1:



Catalytic Properties

FEZA21-OR-020

How acidity influences light olefin diffusion in H-SAPO-34 zeolites

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[1]Center for Materials Science and Nanotechnology, University of Oslo, Oslo, Norway, [2]Center for Molecular Modeling, Ghent University, Zwijnaarde, Belgium, [3]School of Materials Science and Engineering, Nankai University, Tianjin, China

Abstract Text:

Acid zeolites or zeotypes are widely used for catalytic and environmental applications thanks to their unique shape selectivity properties. The product distribution of zeolite-catalyzed conversions is typically the result of a complex interplay of intrinsic reactivity, stabilization of crucial intermediates and transport phenomena. [1,2] Diffusion limitations in confined zeolites may have a significant impact on the ultimate product selectivity and separation. Quantifying the adsorption and diffusion behavior is extremely challenging due to the simultaneous occurrence of multiple phenomena at different length and time scales. As such, a combined experimental and theoretical approach is mandatory to properly map the various contributing factors.

In the context of the methanol-to-olefins (MTO) conversion, experimental studies reported a strong correlation between the product distribution and product diffusivity. [2,3] The MTO process is characterized by a complex reaction environment in which both oxygenate species (water, methanol,…) as well as aromatic and aliphatic hydrocarbon pool (HP) compounds are present in the zeolite pores. Consequently, the transport of hydrocarbons and loading of the catalyst cages evolves dynamically with time on stream. However, the true impact of the presence of guest molecules and the acid site density of the framework on the diffusion characteristics of small hydrocarbons in small-pore zeolites remains unclear.

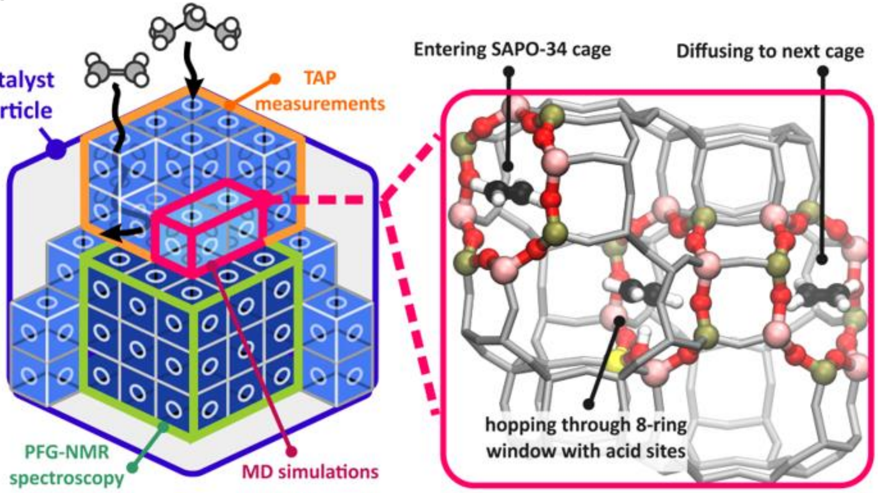
In this contribution, we present novel insight into the diffusion behavior of light olefins (ethene, propene) and paraffins (ethane, propane) in H-SAPO-34 zeolites with a varying acid site density and loading of entrapped guest molecules using a complementary set of computational and experimental techniques (Image 1). SAPO-34, a common catalyst for MTO conversion, can be regarded as a supramolecular system consisting of spacious cages which are connected by small 8-ring windows through which diffusion takes place as a hopping event. [4]

Ab initio molecular dynamics (MD) simulations are performed to characterize individual hopping events at *operando* conditions. Since diffusion of small hydrocarbons is a hindered process, umbrella sampling simulations are carried out to construct free energy profiles and extract diffusion coefficients. The current approach by combining first-principle simulations and enhanced sampling techniques is unprecedented and a major step forward to unravel the role of acidity on the diffusion behavior. [5,6] Finally, computational observations are complemented by PFG-NMR spectroscopy (to probe intracrystalline diffusivities) and pulse-response temporal analysis of products (TAP) measurements (to probe external surface interactions and internal pore diffusion).

Our results clearly demonstrate that the presence of Brønsted acid sites on the 8-ring windows has a beneficial effect on the transport of olefins while the diffusion rate of paraffins remains invariant for the acid site density. The observation that alkenes can enter more deeply inside the zeolite crystals and diffuse faster through the pores can be ascribed to the formation of favorable π-H interactions with the acid protons. On the other hand, the diffusion process may be severely hampered by a higher loading of alkenes or aromatic HP species. Since the concentration of aromatics increases as the catalyst ages, the spatiotemporal distribution of the HP species will have a non-negligible impact on the product diffusivities. These remarkable findings may lead to the synthesis of zeolites with dedicated acid site distributions to promote either the transport of alkenes or alkanes, opening up new perspectives for tuning the catalytic selectivity or for olefin/paraffin separation purposes.

We thank the ERC (Consolidator Grant 647755) for financial support. Computational resources were provided by the Flemish Supercomputer Center, funded by Ghent University, FWO and the Flemish Government.

Image 1:



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Catalytic Properties|Zeolites/Inorganic materials

FEZA21-OR-022

Hydroisomerization of n-heptane over Pt/SAPO molecular sieves: The impact of metal-acid proximity

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Abstract Text: Introduction

Bifunctional catalysts play a significant role in modern petroleum refining [1]. In these catalysts a metal (sulfide or oxide) function and a solid acid site are combined for the conversion of carbonaceous feedstocks into clean diesel and jet fuel. Alternative feedstocks such as biomass and waste can also be used, providing liquid fuels via the Fischer-Tropsch process [2].

Catalysts for hydroisomerization of the linear alkane feedstock to branched alkanes are composed of supported platinum nanoparticles and zeolites. The platinum catalyzes (de)hydrogenation of the alkanes and alkenes, and the acid sites of zeolites allow for isomerization and cracking. Research on these catalysts focuses on metal particle size, solid acid architecture and the metal-to-acid site ratio. In the 1950's it became accepted, according to Weisz's "intimacy criterion", that the closest proximity between metal and acid sites results in the highest catalytic activity and selectivity [3]. However, more recently, research performed on Pt/alumina/zeolite-Y catalysts shows that closest proximity between the active sites can be less favorable for isomer selectivity [4].

In this work, we extended the study on metal-acid proximity towards silicoaluminophosphate (SAPOs) molecular sieves as acid function. SAPO-11 with a one-dimensional micropore structure and 10 membered rings was used, together with Pt and γ-Al_2O_3 as binder. The Pt particles were selectively located on the SAPO-11 crystals or further from the acid sites on the alumina binder using different Pt precursors [4]. These catalysts were evaluated for both *n*-heptane and *n*-hexadecane hydroisomerization.

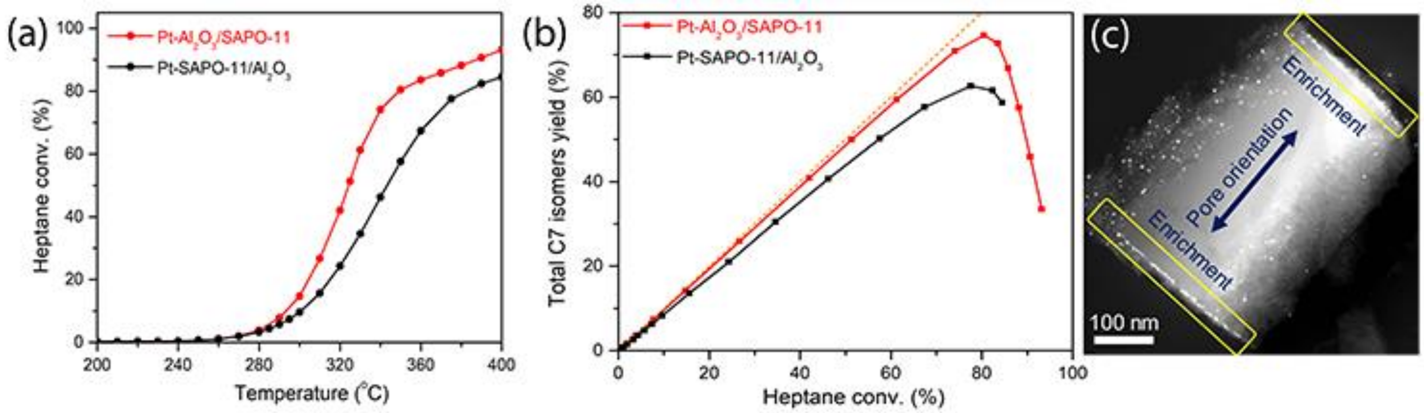
Results and discussion

The distribution of platinum particles in each catalyst was studied by transmission electron microscopy (TEM). The average size of the metal particles in Pt-Al_2O_3/SAPO-11 (Pt on binder) was 1.8 nm and showed a narrow distribution, while the average Pt particle size of Pt-SAPO-11/Al_2O_3 (Pt in/on SAPO-11) was around 3.6 nm with bimodal distribution. ICP measurements showed that the Pt loading on both catalysts was approximately 0.6 wt %. The NH_3-TPD suggested that the acid density and strength were also similar for these two catalysts. Therefore, the main variable in these catalysts was the location of the Pt particles on either the alumina binder or on/in SAPO crystals. For *n*-heptane conversion, Pt-Al_2O_3/SAPO-11 catalysts showed higher activity (Figure 1a) and higher isomer yields (Figure 1b) than the Pt-SAPO-11/Al_2O_3 catalysts.

HAADF-STEM imaging of an ultramicrotomed Pt-SAPO-11 catalyst revealed that the vast majority of platinum particles with large sizes were present on the outside of SAPO-11 crystals, and a fraction of smaller platinum particles were embedded inside SAPO-11 crystals (Figure 1c). Locating a fraction of Pt particles inside the porous solid acid results in pronounced mass transport limitation as is inferred from the lower activation energy for this catalyst (cf. Fig 1a, black dots). In that case, the molecules are more likely to undergo secondary reactions, explaining the higher yield of cracked products. When the Pt is located on the binder however, diffusion of *n*-heptane to Pt sites, heptenes to acid sites and *i*-heptenes to Pt sites is efficient. Therefore, we conclude that locating the Pt particles on the binder is beneficial for the catalyst selectivity.

Image 1: Impact of metal-to-acid site proximity on n-heptane conversion: (a) activity and (b) selectivity over Pt-Al_2O_3/SAPO-11 (red) and Pt-SAPO-11/Al_2O_3 (black); (c) STEM image of an ultramicrotomed SAPO-11 crystal with Pt particles showing enrichment at the pore mouths for sample Pt-SAPO-11/Al_2O_3.

Image 1:



Impact of metal-to-acid site proximity on n-heptane conversion: (a) activity and (b) selectivity over Pt-Al$_2$O$_3$/SAPO-11 (red) and Pt-SAPO-11/Al$_2$O$_3$ (black); (c) STEM image of an ultramicrotomed SAPO-11 crystal with Pt particles showing enrichment at the pore mouths for sample Pt-SAPO-11/Al$_2$O$_3$.

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Catalytic Properties|Zeolites/Inorganic materials

FEZA21-OR-024

Synthesis of hierarchical, macroscopic and bead-shaped Lewis acid zeolites by hydrothermal treatment and subsequent post-synthesis techniques

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Abstract Text: Hierarchical zeolites possessing secondary meso- and macroporosity have shown lower diffusion limitations and superior catalytic performance compared to conventional microporous zeolites.[1] This secondary porosity should be ideally preserved during the shaping step that is required to overcome pressure drop in the large-scale application of the catalysts in fixed bed reactors. Conventionally, zeolites are shaped using extrusion techniques, for which zeolite powders are normally mixed with binders. The presence of binders provides good mechanical strength in extrudates against crushing. However, the binder generally has adverse impacts on the zeolite properties too, e.g. active sites dilution and pore blockage.

Herein, we present the synthesis and catalytic application of bead-shaped (d_{beads} = 0.3 - 0.6 mm) and hierarchical zeolites with both BrØnsted acid sites (framework Al) and Lewis acid sites (Sn, Zr or Hf). Firstly, all bead-shaped zeolites (in Al form) have been synthesized without using any kind of binder by employing a type of polymeric resin beads as hard template (see Fig.1). In the next step, the Lewis acid zeolites were obtained by post-synthesis dealuminatoin of Al-zeolites using different acid concentrations and subsequent insertion of metals such as Sn, Zr or Hf into the zeolite structure.[2] The prepared zeolitic beads were tested in the conversion of dihydroxyacetone into methyl lactates as more valuable chemicals .[3] The results indicate that the crystalline Al-Sn-Beta-beads displayed the highest activity, selectivity (99%) and yield (98%) in the conversion of dihydroxyacetone (DHA) to methyl lactate (ML). These catalytic beads are easily recoverable from reaction medium without any need for extra centrifugation step compared with zeolitic powders and can be used in consecutive runs. They are versatile and have the potential to be used in several reactor designs.

Image 1:

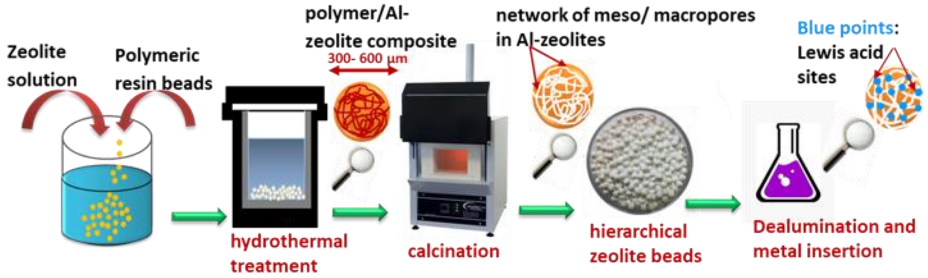
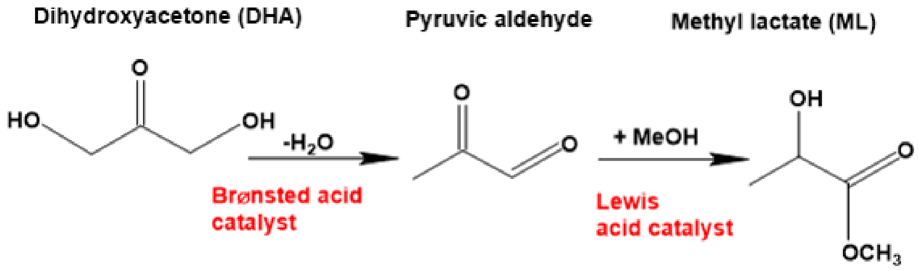


Fig.1- Schematic illustration of Lewis acid zeolite synthesis route

Image 2:



Reaction scheme of dihydroxyacetone conversion to methyl lactate

References: [1] M. Hartmann, Angewandte, 2004, 43, 5880–5882.
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Catalytic Properties|Zeolites/Inorganic materials

FEZA21-OR-025

Molecular elucidating of an unusual growth mechanism for polycyclic aromatic hydrocarbons in confined space

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Abstract Text: The formation of polycyclic aromatic hydrocarbons (PAHs) is inevitable in zeolite-catalyzed processes, especially in industrially important petrochemical processes (catalytic cracking, isomerization, aromatization, etc.) and coal-based chemical processes (such as MTO and syngas conversion). SAPO-34 molecular sieve has been proved to be a preeminent catalyst in MTO industry, yet it suffers a rapid catalyst coking and deactivation induced by the deposition of such detrimental extended aromatic hydrocarbons, which necessitates continuous regeneration operations and poses challenges to practical process design. To alleviate or even prevent catalyst deactivation, unambiguously unravelling of the structural motifs of PAHs and deciphering the molecular route of PAHs formation evolution, at a molecular scale, is necessary.

Tremendous efforts have been made to identify and locate PAHs in catalytic reactions. The conventional Guisnet's method can identify and quantify a large proportion of coke while this method is limited to the analysis of molecules with maximum molar weight below 300 g mol^{-1}. Various sophisticated spectroscopic techniques such as IR, UV-Raman, UV-Vis and NMR spectroscopy, with the merits of being non-destructive and operable *in-situ* or *operando* modes, have also been extensively used. These spectroscopic techniques can differentiate the insoluble, highly condensed PAHs from the soluble, light constituents, yet, they fail in determining the molecular structure of the insoluble fraction of coke.

Herein, we first proposed an effective strategy through integrating a state-of-the-art matrix-assisted laser desorption/ionization Fourier-transform ion cyclotron resonance (MALDI FT-ICR) mass spectrometry (that is traditionally applied for deciphering the structure of biological molecules) with isotope labeling technique (Fig. 1). With this strategy, we can definitively identify, at a molecular scale, the chemical nature of the heavier PAHs formed in an industrially important methanol-to-olefins process as a model reaction. We provided, for the first time, a cage-passing growth mechanism for PAHs in confined spaces from both qualitative and quantitative view. The molecular evolution route evolves from occluded long chain olefins seeds growing to soluble lighter PAHs (ranging from naphthalene to pyrene), and eventually clustering to insoluble heavier PAHs (cross-linked multi-core PAHs with graphene-like structure in this work). And on this basis, two pyrolysis mechanism of the PAHs (fracture between cages and corrosion in-cage) under steam condition have been proposed. As a proof of concept, cage-passing growth mechanism was validated on other cage-structured zeolites, and is expected to be a general C-C assembly mode for PAHs growth in zeolite- or molecular sieve-catalyzed reactions (Fig. 2). Such a mechanistic motif unveils the significance of host-guest chemistry in catalysis field and would help in resolving the long-standing scientific puzzle of how to identify the chemical nature of PAHs. The cross-linked multi-core molecular structure of PAHs identified here resembles the structure of petroleum asphaltene, coal, and soot formed in fuel combustion process. These common features enable the unifying description of chemical structure motif of a large category of extended PAHs as biphenyl- and/or alkyl group-bridged, three dimensionally cross-linked multi-core aromatics. These insights would help in establishing the molecular structural evolution of carbonaceous matter in much broader chemistry fields.

Image 1:

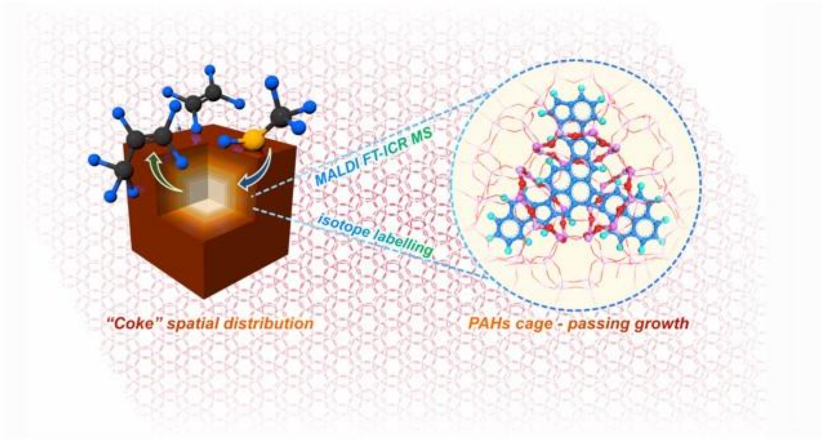
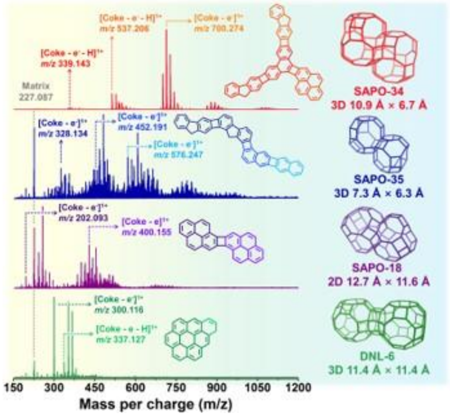


Image 2:



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Catalytic Properties|Zeolites/Inorganic materials

FEZA21-OR-026

Increase of alkene-based cycle contribution in MTO processes by regulating aluminium locations in zeolite lattice sites

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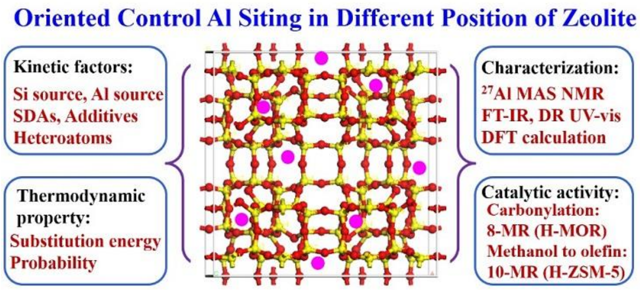
Abstract Text: Methanol is expediently produced via syngas ($CO+H_2$) from multifarious carbon sources such as coal, natural gas and biomass, and it is an important platform species for the formation of various hydrocarbons. Design and development of high-efficient zeolite catalysts are crucial for the conversion of methanol to various desired products, such as olefins (MTO), propene (MTP) and aromatics (MTA). Through modifying the pore structure, adjusting the acidity and altering the morphology, the catalytic activity and target products selectivity as well as the relative contribution of alkene-based cycle to aromatic-based cycle of zeolite-based catalysts for methanol conversion can be controllably tailored and finely tuned (as shown Figure 1).

Among them, acid sites distribution is an important factor that affect the catalytic performance of zeolites in methanol conversion. The different Al siting in framework could alter the local environment and shape-selectivity of active acid sites, leading to the variation of reaction mechanism and product distribution. It was found that MCM-22 zeolite has three types of pore structures, i.e. supercages, sinusoidal channels and side pockets, where increasing the acid sites in the sinusoidal channels can markedly promote the contribution of alkene-based cycle and produce more propene (as shwon in Figure 2).

Recently, we also demonstrated that acid sites distribution can be regulated by modifying the synthesis conditions, using certain post-synthesis treatment methods or incorporation of heteroatoms in synthesis gel. For examples, Al atoms are enriched in the sinusoidal and straight channels of H-ZSM-5 zeolite synthesized from silica sol, whereas for H-ZSM-5 prepared from TEOS, Al atoms are mainly located in the intersection cavity. ^{12}C/^{13}C methanol stiwiching experiment indicates that the acid sites in sinusoidal and straight channels are more encouraging for the alkene-based cycle and accelerating the production of propene.

However, the addition of Na^+ and/or Li^+ in the synthesis gel elevates the fraction of Al sited in the intersection cavity of H-ZSM-11 that promotes the aromatic-based cycle and produces more ethene and aromatics. Selective removal of Al atoms in external pockets by oxalic acid or citric acid treating markedly increased the catalytic stability of H-MCM-22 in MTO. Meanwhile, various high-efficient MTP catalysts (B-Al-ZSM-11, B-Al-MCM-22 and Ge-Al-ITQ-13) were obtained through improve the contribution of alkene-based cycle by adding proper content of B or Ge in synthesis gel, as the competitive occupancy of various framework T sites between the heteroatoms and Al atoms. Therefore, regulation of the Al siting in zeolite framework is crucial for tailoring the activity and selectivity of zeolite-based catalysts for acid catalyzed reactions.

Image 1:



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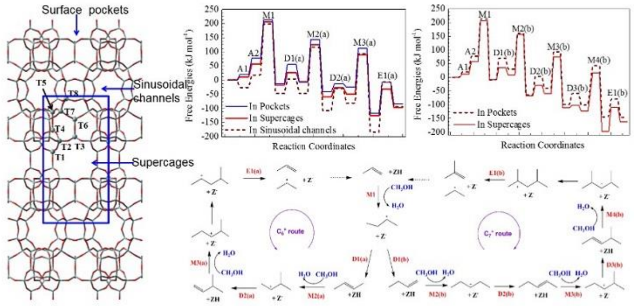

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Catalytic Properties|Zeolites/Inorganic materials

FEZA21-OR-027

Methane to methanol conversion over Cu-zeolites - structure performance relationships

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Abstract Text:

A process allowing energy-effective methane to methanol (MTM) conversion would represent a major breakthrough for the chemical industry. Cu-exchanged zeolites have been shown to possess active Cu sites able to cleave the C−H bond of methane at temperatures ≤ 200 °C, enabling the stoichiometric transformation of methane into methanol [1]. The conversion is performed through a stepwise process, involving high-temperature activation in O_2 to generate the active sites, methane loading at 200 °C, and steam-assisted methanol extraction.

We have combined DFT calculations with laboratory performance testing and in situ/operando Cu K-edge XAS to establish structure-activity relationships for the MTM conversion over a series of Cu loaded zeolites with different topologies [2,3,4]. By operando XAS, we tracked the oxidation state and average coordination of Cu ions during each step of the process and explored the impact of different pretreatments and compositional characteristics such as Cu loading and Si/Al ratio. With DFT, we have investigated the reactivity of a wide range of potential active sites for the reaction.

We employ high-temperature reaction with O_2 to form the active Cu(II) sites, which then undergo reversible redox chemistry during the CH_4-loading and CH_3OH extraction steps. For Cu-CHA, we identified a positive linear correlation between the methanol productivity and the composition-dependent self-reducibility under high-temperature treatment in He, allowing us to rationalize the impact of the sample composition on the productivity for the MTM conversion. The most recent research efforts on Cu-MOR have highlighted the crucial role of operating at consistent conditions for both spectroscopy and performance testing. Having fulfilled this requirement, aided by high-energy resolution XANES and multivariate analysis [5,6], we unambiguously assessed the nuclearity of the active Cu site in the investigated series of Cu-MOR materials. We are able to fully rationalize our observations assuming a dimeric copper site as the active species in MOR, and this is further corroborated by DFT investigations.

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Catalytic Properties|Zeolites/Inorganic materials

FEZA21-OR-028

Strong Brønsted Acid Site Accessible from Large 12-ring Pore in YFI Type (YNU-5) Zeolite

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Abstract Text: Strong Brønsted acid sites tend to be generated in small pores[1)]. Quantum chemical calculations show that smaller Al-O distance, readily found on walls of small pores, induces strong acidity[2)]. However, generation of strong Brønsted acid sites in large pores is strongly demanded for efficient conversion of heavy oil components, bio-derived resources, and naphthalene and other polycyclic compounds. Nakazawa and Kubota et al. recently synthesized YNU-5 zeolite (YFI type) with stability in acidic conditions[3)]. The YFI type framework has independent 8-ring separated from spaces consisting of 12-ring by a silicate wall with one atomic layer thickness (Figure 1). It is expected that protons on this wall has strong acidity induced by the small pore size and to be accessible from 12-ring. Here we report, on the YFI type zeolite, the presence of strongest Brønsted acid sites among those accessible from large micropore (12-ring).

NH_4-YNU-5 with [Al] = 1.4 mol kg^{-1} (Si/Al molar ratio = 11) was synthesized[3)], and dealumination was carried out in 2 mol dm^{-3} nitric acid solution to obtain a deAl-YNU-5 with [Al] = 0.32 mol kg^{-1} (Si/Al = 51)[4)]. The ammonia IRMS-TPD measurements were carried out after pretreatments in oxygen at 813 K as described elsewhere[1)]. On the other hand, after the pretreatment in oxygen at 813 K, the sample was exposed to pyridine vapor (pressure at room temperature) and then exposed to ammonia at 353 K with recording IR spectra on these steps.

The ammonia IRMS-TPD of the pretreated NH_4-YNU-5 (hereafter, in-situ H-YNU-5) showed only Brønsted (not Lewis) acidity. The number of Brønsted acid sites was 1.1 mol kg^{-1}, close to [Al], showing high quality of the sample. Distribution of standard ammonia desorption enthalpy[1)] is shown in Figure 2 (left). The distributions on other zeolites with similar [Al] are also shown, and on MOR, the distributions in 8- and 12-rings are identified[5)] based on the different wavenumbers of acidic OH groups[6)]. The Brønsted acid strength was *BEA < MOR (12-ring) < MFI < MWW ≈ YFI < MOR (8-ring). As shown in Figure 2 (right), the in-situ H-YNU-5 showed a band ascribed to stretching of the acidic OH groups at 3607 cm^{-1}. The band almost completely diminished with exposure to pyridine vapor, and simultaneously formation of pyridinium cation was observed. Thus, pyridine was observed to react with most of the Brønsted acidic OH groups detectable by IR. Then, introduction of ammonia caused little change of the IR spectrum in the OH stretching region, demonstrating that all the OH groups were accessible with not only ammonia but also pyridine. On the deAl-YNU-5, similar results were obtained. The molecule of pyridine is estimated to be larger than 8-ring, indicating that most of the Brønsted acid sites were accessible from the 12-ring or external surface. Enrichment of such dense (2.4 sites unit $cell^{-1}$) Brønsted acid sites close to the external surface is not probable, and therefore, it is concluded that most of the Brønsted acid sites on YFI were accessible from 12-ring.

It has been known that protons can hop between oxygen atoms[7)]. On the other hand, potassium cations were found in the independent 8-ring in as-synthesized and calcined forms of YNU-5[3)], indicating that the oxygen atoms having ion exchange function, at least a part of them, face to the independent 8-ring in these forms. It is probable that some of protons face to the independent 8-ring, but even bulky molecules can react with them from the side of 12-ring, because there is only a thin layer between the 8- and 12-ring pores.

To the best of our knowledge, only weak Brønsted acid sites had been found in 12-rings, as those on *BEA and MOR (12-ring) shown above. It has thus been found that the YFI type zeolite has the strongest Brønsted acid sites among those accessible from large micropore (12-ring).

Acknowledgement: This study was partly supported by JST, CREST (JPMJCR17P1) and JSPS, KAKENHI (16H04568).

Image 1:

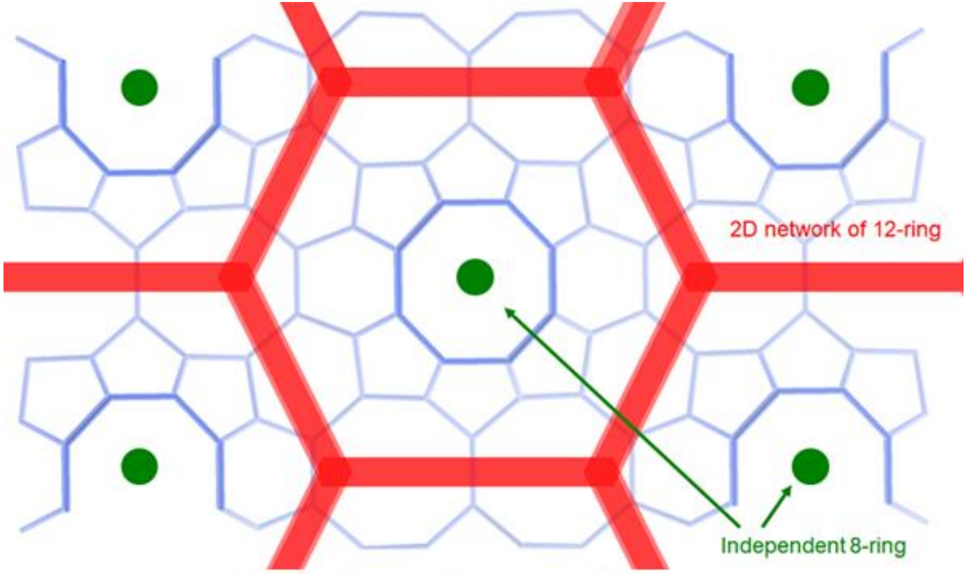

Figure 1: YFI framework viewed along c-axis.

Image 2:

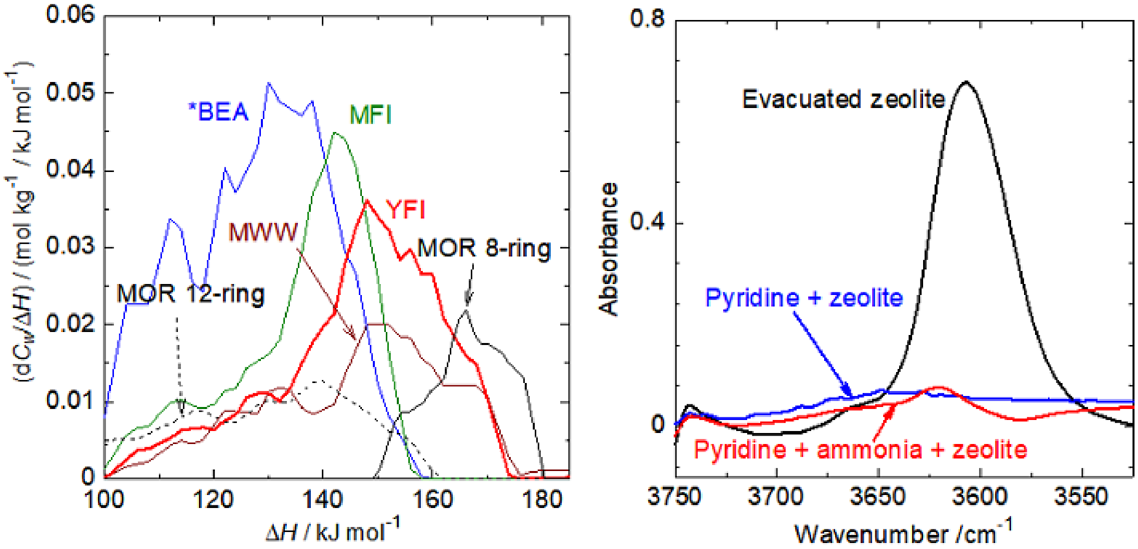

Figure 2: (Left) Distribution of strength (ΔH, standard enthalpy of ammonia desorption) of Brønsted acid sites accessible by ammonia of zeolites with various framework topologies and around 1 mol kg^{-1} of [Al], and (Right) IR spectra of NH_4-YNU-5 (YFI type) zeolite after pretreatment (i.e., in-situ H form, black), followed by exposure to pyridine vapor (blue) and subsequent exposure to ammonia (red).

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Catalytic Properties|Zeolites/Inorganic materials

FEZA21-OR-030

Promotion of zeolite-catalyzed methanol dehydration to DME by organic additives

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Abstract Text:

Introduction

Zeolites are an extremely important class of catalysts widely used in industry. As inorganic microporous solids their ubiquitous presence stems from their robust nature and ready applicability. The solvent-like confinement effect of the zeolite micropores stabilizes intermediates and lowers the energy of transition states in key reaction steps [1]. Organo-catalysis by guest species in the zeolite micropores offers the potential to modify their catalytic properties [2]. Zeolites can be used as catalysts for the dehydration of methanol to dimethyl ether (DME). We have discovered that a wide range of organic carbonyl compounds and their derivatives (carboxylate esters, carboxylic acids, ketones, ketals, aldehydes and acetals) enhance the catalyst productivity for the formation of DME [3].

Materials and Methods

A wide range of zeolites and non-microporous solid-acid materials were tested as catalysts for the methanol dehydration to DME. As part of this work the impact of organic additives on catalyst performance was studied under relatively mild conditions (150 °C and a methanol partial pressure of 110 kPa). These relatively mild conditions allow any significant methanol to hydrocarbon chemistry to be negated, with a high reaction selectivity to DME. The methanol dehydration reactions were carried out using a 16-channel parallel fixed-bed stainless steel reactor system. In a typical experiment each reactor housed a 25 mg bed of catalyst (having particle size fraction of 100 to 200 microns diameter) with pre- and post-beds of an inert material (carborundum) and was maintained at a temperature of 150 °C. A gaseous feed comprising 10 mol% methanol, a variable concentration of a co-feed compound and inert gas (nitrogen and helium) was introduced to all 16 reactors. Throughout the experiments the weight hourly space velocity (WHSV) of methanol was maintained at 17.1 h^{-1} and the partial pressure of methanol maintained at 110 kPa. The effluent stream from each reactor was diluted with inert gas (nitrogen) and was periodically analysed by online gas chromatography to determine the yield of dimethyl ether product.

Results and Discussion

Promotion of DME yield from the methanol dehydration reaction over zeolite catalysts has been observed when co-feeding organic carbonyl compounds. Figure 1 shows the DME productivity of a ZSM-5 catalyst when co-feeding different methyl carboxylate esters. At a concentration of 5 mol% relative to methanol, the promotion of the DME productivity increase with the size of the ester co-feed. In our studies we have observed promotion of the DME yield over many different zeolites with a range of framework structures and over 50 different additives. Tuning the combination of catalyst and additive allow large promotions in DME productivity to be achieved. We have observed promotion at concentration as low as 10 ppm, relative to MeOH, and increases in DME productivity by a factor of over twenty. The promotion can be readily and cleanly reversible, allowing switching of promoters in the same experiment and the promoter concentration can be used to fine tune the productivity of different zeolites for making DME from methanol.

Significance

Methanol chemistry with zeolites is subject of studies by many academic and industrial research laboratories with the aim of understanding the mechanism of its industrially important conversion to hydrocarbons and DME. The use of organic carbonyl compounds as additives to promote the formation of DME from methanol with zeolite catalysts is a potentially important effect in zeolite catalysis that has not previously been recognized. This work shows how the well known 'confinement effect' in zeolite catalysis can be further exploited to great effect when appropriate reaction conditions are used.

Image 1:

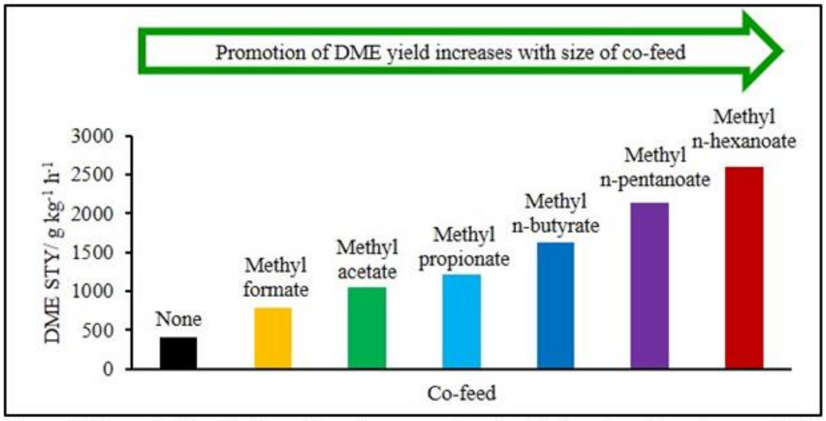

Figure 1. Impact of co-feeding a homologous series of methyl carboxylate esters on DME space-time yield (STY) of ZSM-5 catalyst. Conditions: 150 °C, methanol WHSV 17.1 h^{-1}, methanol partial pressure 110 kPa, methyl ester partial pressure 5.5 kPa.

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Catalytic Properties|Zeolites/Inorganic materials

FEZA21-OR-031

CO2 hydrogenation to chemicals: adjusting final product distribution by selecting zeolite structure and crystal size

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Abstract Text:

The use of CO_2 as a renewable carbon source for the production of commodity chemicals (light olefins, aromatics, liquid fuels or carboxylic acids, among others) is a topic of increasing interest. A rather immediate alternative is the incorporation of CO_2 to synthetic gas streams for its conversion to hydrocarbons and long-chain alcohols, taking advantage of the knowledge and technology associated with the Fischer-Tropsch Synthesis (FTS) process in the presence of conventional FTS catalysts based on iron oxides [1]. These catalysts are active for both, partial reduction of CO_2 to CO through the RWGS, and formation of hydrocarbons via the FT reaction. In any case, this indirect route of hydrocarbon formation from CO_2 presents an important energetic cost and traditionally uses H_2 coming from reforming processes, which also have an important generation of CO_2 associated.

Thus, the development of efficient technologies for direct CO_2 conversion would be highly desirable. However, the inertness of this molecule and the high kinetic barriers related to its participation in C-C formation reactions [2], has limited its use as a C1 building block, and its direct conversion to hydrocarbons with more than two carbons (C_{2+}), although intensively studied in the last years, still remains a major challenge.

Two different approaches have been proposed for the conversion of CO_2 into C_{2+} hydrocarbons of interest: the methanol mediated pathway and the FTS route [3]. The former combines the conversion of CO_2 to methanol on transition metal oxide based catalysts (i.e. In_2O_3, Cr_2O_3) with the methanol-to-olefins (MTO) or aromatics (MTH) chemistry on acid zeolites (i.e. CHA, MFI). Although the MTO/MTH process is well known and can be effectively applied, methanol yields in the first part of the tandem process are low, limiting the final hydrocarbon productivity. CO_2 conversion processes via FTS on K-promoted Fe_3O_4 are more active and present lower selectivity to CO and methane. Here, CO_2 is converted into CO via reverse water gas shift (RWGS route) followed by the conversion of CO to hydrocarbons by a classical FTS mechanism. Coupling of the FTS catalyst with the adequate zeolite will allow for product redistribution and selective production of olefins, aromatics or isoparaffins.

In this work, we have studied the influence of zeolite structure and crystal size on the conversion of CO_2 on multifunctional catalysts combining K/Fe_3O_4 with different zeolites. Experiments have been performed in a fixed bed reactor at T=320ºC, P=25 bar, WHSV=7 h^{-1}, H_2/CO_2=3 mol/mol. Under those conditions, 100 ml/min H_2 + 32 ml/min CO_2 + 8 ml/min N_2 (as internal standard) is fed to 1 g of catalyst (0.5 g K/Fe_3O_4 + 0.5 g of zeolite). Three different zeolite structures have been compared, MFI, BEA and CHA. Micron- and nano-sized chabazite, nano-beta and nano-ZSM-5 were synthesized in house. The two latter were compared with commercial beta (CP814E) and ZSM-5 (CBV2314), and all samples present similar composition (Si/Al~10-15).

As expected, addition of the zeolite does not affect CO_2 nor the overall selectivity to CO and hydrocarbons. However, hydrocarbon distribution is affected by the zeolite structure. Thus, chabazite and beta increase the C_1-C_4 hydrocarbon yield, whereas MFI increases the yield to C_{5+} hydrocarbons. At short times on stream (TOS) all zeolites present low C_2-C_4 olefin selectivity. During this early stage of the reaction, hydrogen transfer reactions will be favored on the fresh zeolites, highly active. At longer TOS the selectivity to olefins is recovered except for ZSM-5. ZMS-5 leads to the formation of aromatics in C_{5+}, whereas chabazite and beta increase the C_2-C_4 yield with high olefin selectivity. Finally, reducing crystal size results in higher yields to light olefins.

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Catalytic Properties|Zeolites/Inorganic materials

FEZA21-OR-032

Shape Selective C-H Activation of Aromatics to Biarylic Compounds Using Molecular Palladium in Zeolites

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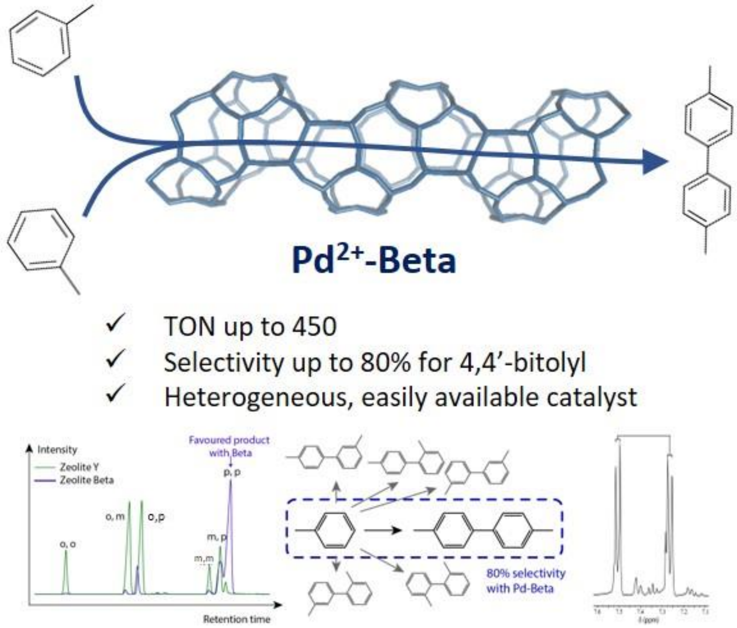
Abstract Text: Biarylic bonds are important structural motifs in numerous organic chemicals. Their current industrial production relies on traditional coupling reactions (Suzuki, Ullmann…), which use pre-activated arenes (aryl halides, arylboronic acids…). The high cost of these intermediates and the associated waste generation usually direct their application towards high-end, specialty chemicals. Especially in the polymer industry there is a growing demand for biarylic monomers because of their superior chemical and physical stability, and their favorable health and safety profile [1-3].

Direct functionalization of unreactive C-H bonds *via* transition metal mediated C-H activation has emerged as a promising alternative to traditional multi-step approaches [4]. C-H/C-H arene-arene couplings can in principle be used for the direct synthesis of biaryls from simple arenes, with e.g. Pd carboxylates as the catalysts [5,6]. If O_2 is used as the oxidant, water is the only by-product. Unfortunately, the multitude of C-H bonds present in organic reactants, and the poor differentiation between them often result in poor regioselectivity. Consequently, reactions with 'simple' arenes (e.g. toluene) lead to useless mixtures of many isomers [7].

A so far unexplored option is to implement the molecular mechanisms of transition-metal catalyzed C-H activation in the shape selective confinement of a porous material like a zeolite. The molecular dimensions and shape of the pores may direct the selectivity to particular products via the imposed steric constraints. This shape selectivity has been extensively studied for acid catalyzed reactions. However, zeolites have so far not been used to create a shape selective environment around molecular catalysts that activate C-H bonds of arenes to form more complex organics. Here we demonstrate that Pd(II) catalysts, site-isolated in the framework of zeolite Beta or some other 12-membered ring (MR) zeolites, uniquely allow to oxidatively couple toluene and other monosubstituted aromatics to biaryls, with exceptional selectivity for the *p*,*p*'-dimer.

Image 1:



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Catalytic Properties|Zeolites/Inorganic materials

FEZA21-OR-033

A Theoretical Parameter Connecting Cavity Architecture, Confined Hydrocarbon Pool Species, and Olefin Distribution in the Methanol-to-Olefin Reaction Catalyzed by Small-Pore Cage-Based Zeolites

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Abstract Text: The methanol-to-olefins (MTO) reaction is one of the most successful processes to produce light olefins ($C_2^=$-$C_5^=$) at an industrial scale. The catalysts used are considered dual systems comprising an inorganic acid zeolite framework and organic compounds hosted inside that constitute the so-called hydrocarbon pool (HP). Olefins are formed by successive methylation and cracking of the HP intermediates, mainly aromatic poly-methyl-benzenes (PMB) initially formed from methanol during an induction period and confined within the cavities of small pore zeolites like CHA, AEI or RTH. The mechanism includes two possible competitive routes: the side-chain pathway involving exo-alkylation of PMB intermediates followed by side-chain elimination, yielding ethene and propene, and the paring cycle comprising an initial ring contraction followed by ring expansion of poly-methyl-cyclo-pentenyl (PMCP) cations, resulting in the preferential formation of propene and butenes (Figure 1).

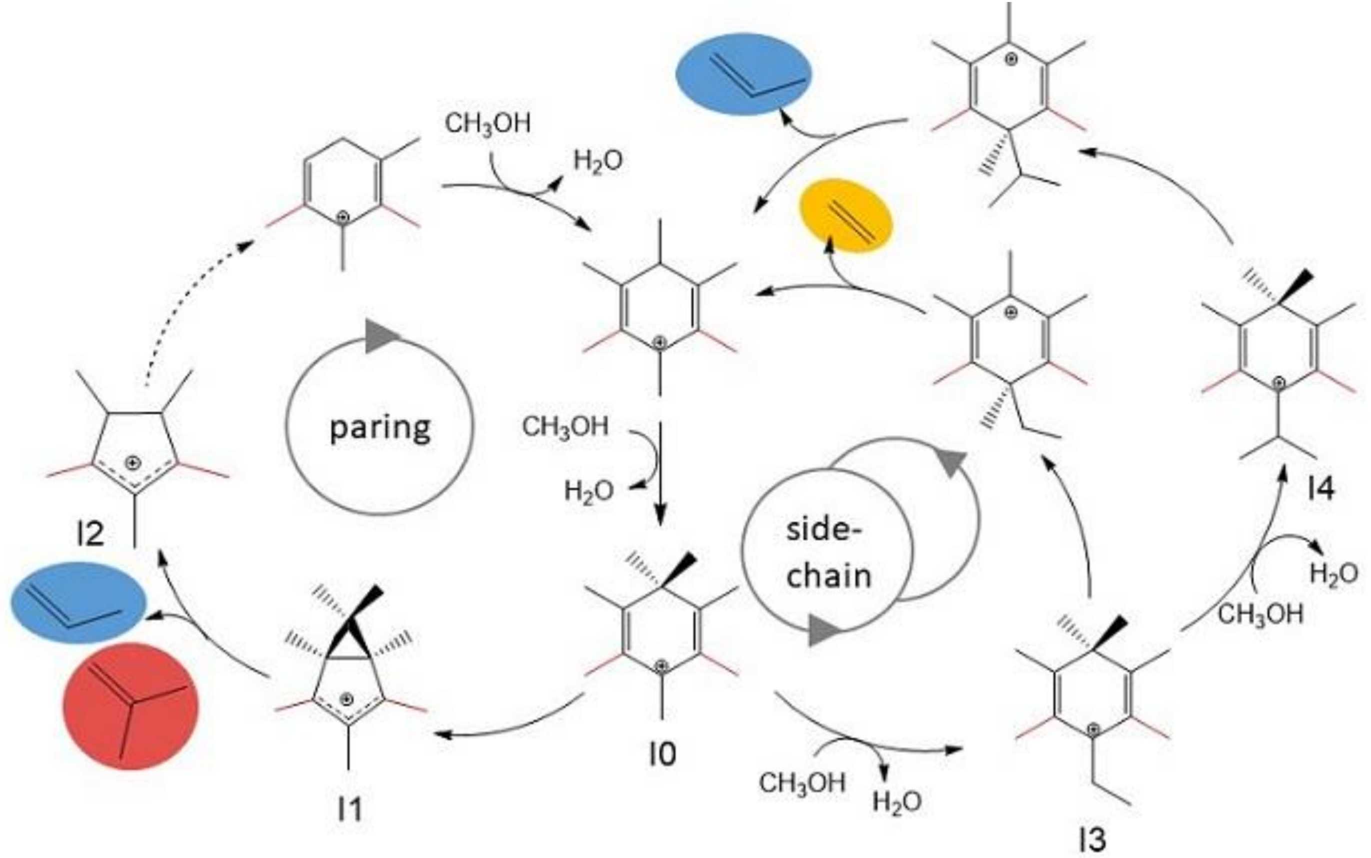
The contribution of each of the two pathways to the global reaction determines the product distribution, that is, the propene/ethene ($C_3^=/C_2^=$) and butene/ethene ($C_4^=/C_2^=$) ratios. Based on a detailed DFT study of the paring mechanism and of the specific host-guest interactions taking place in different zeolite frameworks, we show that there is a correlation between the zeolite cavity architecture, the degree of methylation of the most abundant entrapped PMB cations and the selectivity to propene and ethene.The relative stabilization (or interaction energy ratio $E_{int(7/5)}$) of penta- and hepta-methyl-benzenium cations in different zeolite cages is proposed as a quantitative parameter able to predict the contribution of the paring route, and therefore the product distribution of the MTO reaction, in small-pore cage-based zeolites (Figure 2).

In a second step, this approach is extended to explain the influence of framework composition and flexibility on the product distribution obtained in silicoaluminophosphates like SAPO-34 and SAPO-18.

Figure 1. Proposed MTO mechanism including the paring and side-chain routes.

Figure 2. DFT calculated energy profile for the paring route in different zeolites (left) and correlation between experimental $C_3^=/C_2^=$ ratio and $E_{int(7/5)}$ parameter.

Image 1:



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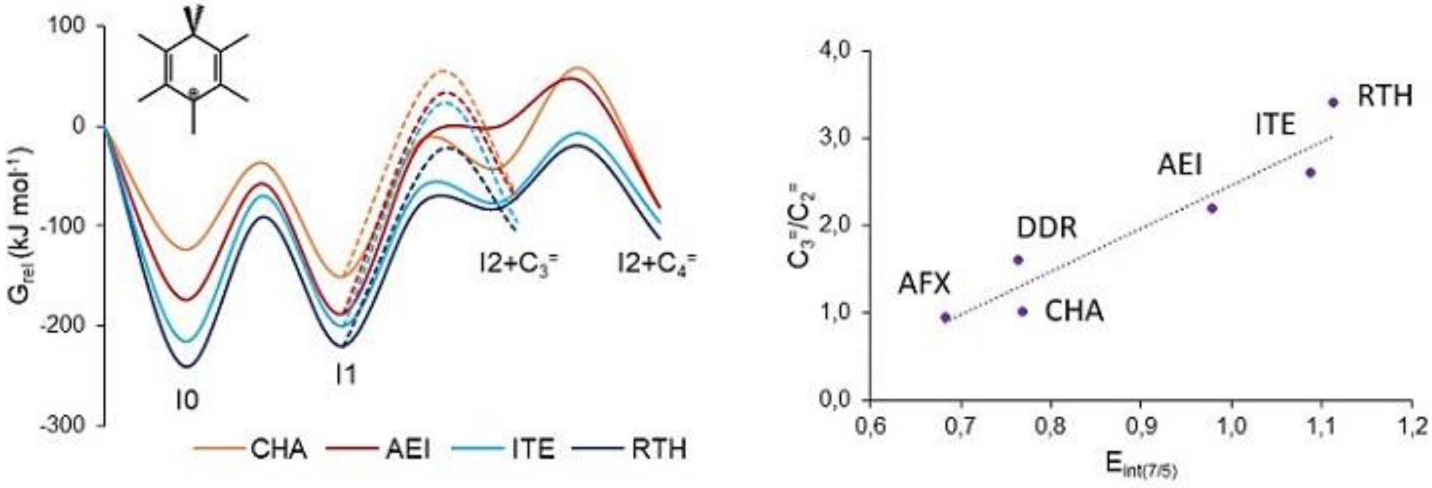

References: 1. Ch. Li, C. Paris, J. Martínez-Triguero, M. Boronat, M. Moliner, A. Corma, Nature Catalysis. 1, 547-554 (2018).

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Catalytic Properties|Zeolites/Inorganic materials

FEZA21-OR-034

Spatially orthogonal chemical functionalization of a hierarchical pore network for catalytic cascade reactions

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Abstract Text: Cascade reactions are sequential chemical transformations in which the starting substrate undergoes a reaction whose product becomes the substrate for the next step, and so on, until a stable product is reached.[1] Cascades offer great advantages in respect of atom economy, and time, labour and resource efficiency management, whilst permitting the use of synthetically enabling intermediates that may be impractical to isolate. However, catalytic cascades, in which the product of a reaction catalysed by species A undergoes a subsequent distinct transformation catalysed by a second species B, are hindered by the possibility of undesired interactions between the initial substrate and the second active site, or indeed between the two catalytic species. Such highly desirable ‘one-pot’ catalytic cascades necessitate the spatial separation of each catalytic step. Here we describe a general route to a new class of spatially orthogonal (i.e. mutually exclusive) bifunctional porous materials,[2] via stepwise detemplation/functionalisation of a hierarchically interconnected silica framework, which permits the chemical environment of macropores and mesopores to be independently tuned. The hierarchical nature of our pore networks regulates active site accessibility and communication between different spatially localised catalytic functionalities.

Spatial compartmentalization of 2.4 nm Pt NPs within hydrophilic mesopores and 5.5 nm Pd NPs within hydrophobic macropores was verified by HAADF-STEM imaging (Fig. 1) and tomography, and EDX. The catalytic advantage of spatially segregating Pt NPs within mesopores, accessible through interconnected Pd containing macropores, is demonstrated for the cascade selective oxidation of cinnamyl alcohol → cinnamaldehyde → cinnamic acid (Fig. 2), the latter an important flavouring. Pd is highly selective towards cinnamyl alcohol oxidation to cinnamaldehyde but promotes decarbonylation of the aldehyde product; in contrast, Pt favours undesired hydrogenation of cinnamyl alcohol via reactively-formed surface hydrogen but is highly selective for cinnamaldehyde oxidation to the desirable cinnamic acid product. Spatial compartmentalization within separate but interconnected pore networks, permits control over the reaction sequence, conferring an order of magnitude enhancement in cinnamic acid yield.

Image 1:

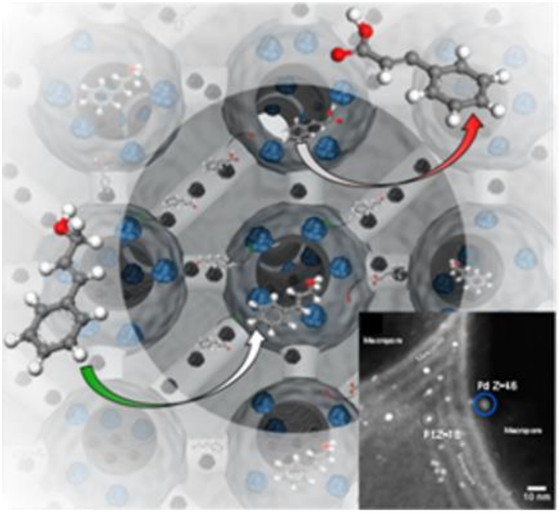

Figure 1. Concept of spatially orthogonal catalysts, with inset HAADF-STEM image of spatially compartmentalized Pd and Pt NPs within meso-macro SBA-15.

Image 2:

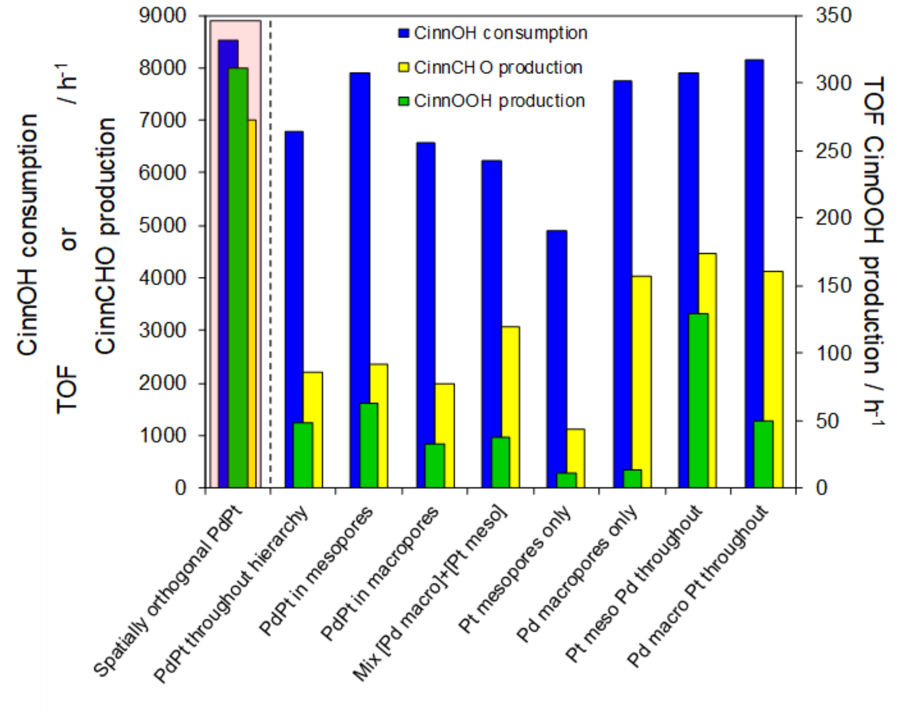

Figure 2. Catalytic cascade aerobic selective oxidation of cinnamyl alcohol to cinnamic acid.

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Catalytic Properties|Zeolites/Inorganic materials

FEZA21-OR-035

Structured Silicalite-1 Encapsulated Ni Catalyst Supported on SiC Foam for Catalytic Dry Reforming of Methane

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Abstract Text: Carbon dioxide (CO_2) and methane (CH_4) co-exist in many sources (*e.g.*, biogas), which are considered the major greenhouse gases. Dry reforming of methane (DRM) has gained much attention due to (*i*) the co-utilisation of CO_2 and CH_4 to reduce the emission of two greenhouse gases and (*ii*) the production of syngas (*i.e.,* CO + H_2). However, metal sintering and carbon deposition during DRM at high temperatures (*e.g.,* 700 °C) can lead to the rapid deactivation of catalysts and the physical blockage of the fixed-bed reactors. Therefore, to address the limitations, novel catalysts and processes are needed to progress DRM further.

The conventional method of preparing metal catalysts, such as Ni, was primarily accomplished by impregnation, giving supported bare metal phase which is still prone to sintering and coking. In this work, we developed the strategy to prepare the reforming Ni catalyst via the encapsulation of Ni nanoparticles (NPs) in inorganic siliceous zeolite, i.e. silicalite-1, which provided effective spatial segregation of Ni NPs and improve the activity and stability (*via* anti-sintering). More importantly, the method was extended to develop simple method of direct synthesis of silicalite-1 encapsulated Ni catalysts on open-cell silicon carbide (SiC) foam, as the structured catalyst (Ni@S1-SiC), for intensifying the DRM process.

Comparative TGA and HRTEM characterisation of the fresh and used catalysts showed that the direct encapsulation method provided highly-dispersed Ni nanoparticles with significantly smaller particle sizes, which showed significantly improved anti-sintering ability compared to the catalysts prepared by the conventional impregnation method. The developed structured Ni@S1-SiC catalyst showed high CO_2/CH_4 conversions of >85% and H_2/CO molar ratio of >0.85 at 700 °C, outperforming other control catalysts under study. Additionally, the structured catalyst demonstrated the highest TOF values of ~5.4 and ~2.1 s^{-1} regarding to CO_2/CH_4 conversions, exhibiting excellent stability and low pressure-drop during 100 h ToS reaction.

The developed structured catalysts based on encapsulated Ni and open-cell SiC foams are particularly advantageous for the high-temperature catalysis. Specifically, the encapsulation method prepared well-dispersed metal catalysts with the anti-sintering ability, and the structured foam support enabled high permeability with the intensified transport phenomena, leading to the low pressure-drop (low energy penalty) and anti-coking ability (long catalyst life). The developed strategy can be expanded to tackle the challenging catalysis with similar issues, therefore, being worthy of further investigation and development for practically intensifying high temperature chemical reactions and processes.

Catalytic Properties|Zeolites/Inorganic materials

FEZA21-OR-036

Study of Ni-exchanged FAU, MFI and CHA catalysts shows impact of zeolite properties on the activity of Ni single sites for selective butene dimerization

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Abstract Text:

Introduction

Light linear and monobranched olefins have attracted growing industrial attention as a basic feedstock and important intermediate in the production of polyethene and plasticizers [1,2]. Butene dimerization on heterogeneous Ni based catalysts represents an appealing route to synthesize linear octenes from undervalued cracking fractions. However, the chemical environment and the different Ni species in Ni-aluminosilicates lead to an ambiguity with respect to the nature of the elementary steps in the Cossee-Arlman dimerization mechanism. In this work, we introduce different Ni loadings into FAU, MFI and CHA zeolites by ion exchange. We study the effect of Ni location and loading in comparison to the activity that can be expected by remaining Brønsted acid site (BAS) in the unselective dimerization and oligomerization of alkenes. Zeolite properties such as Al pairs and pore size are shown to have an important impact on the activity and selectivity of Ni-zeolite catalysts in butene dimerization.

Results and Discussion

The butene consumption rates per mol Ni obtained for Ni-H-FAU and Ni-Na-FAU series suggest an exponential decrease of activity with Ni loading (Figure 1B, black full symbols). This indicates that, at higher Ni loadings, a smaller faction of Ni atoms are active, either because of the formation of multinuclear Ni species or because of limited accessibility of Ni sites.

XAFS measurements of the Ni-Na-FAU series (Figure 1A) shows for samples with Ni loadings above 200 $\mu mol \cdot g^{-1}$, the appearance of Ni-Ni scattering indicative of the presence of multinuclear Ni clusters. Conversely, the sample with 50 $\mu mol \cdot g^{-1}$ Ni does not feature the signal for the Ni-Ni distance, leading to the conclusion that Ni is present as isolated Ni^{2+} ions.

While the butene consumption rates are similar for both series, Figure 1B shows that Ni-Na-FAU catalysts are remarkably more selective to linear octenes than Ni-H-FAU materials. This is attributed to the BAS catalyzed dimerization of branched isomers. Activity tests on an H-FAU reference material showed that the butene dimerization rate on BAS is in the range of 6000 $mol_{Butene} \cdot mol_{BAS} \cdot h^{-1}$. Based on this, it can be observed that Brønsted acidity alone does not account for the remarkable improvement of selectivity to linear octenes achieved in Ni-Na-FAU materials and other parameters such as Ni location, accessibility or electronic effects due to Na^+ ions should be examined.

Studies on Ni exchanged CHA with different concentrations of Al pairs shows how the activity increases with Ni loading up to the point all Al pairs are exchanged. This is strong evidence of the nature of the active site being a single Ni^{2+} ion exchanged on Al pairs. Comparison with MFI and FAU series sheds light on the influence of pore size and interconnectivity. Overall, our study provides relevant information on the speciation of transition metal ions in different zeolite frameworks and on how catalytic activity of such metal ions is affected by their local environment and accessibility.

Image 1:

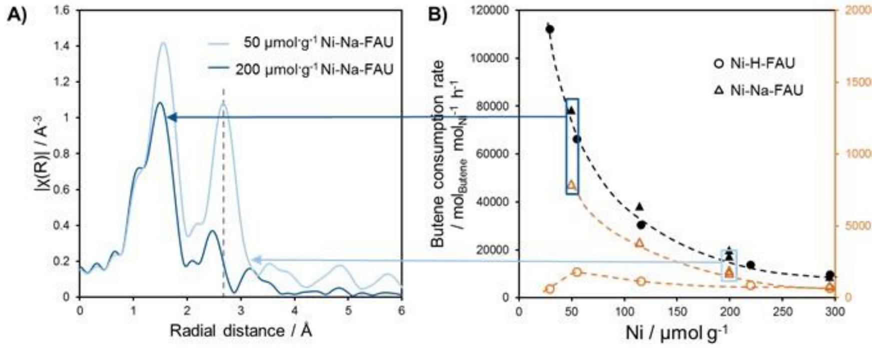

Figure 1. A) XAFS spectra of samples of the Ni-Na-FAU series. Dashed line at ca. 2.7 Å indicates Ni-Ni-scattering. B) Butene consumption rates and octene formation rates per mol Ni for Ni-H-FAU and Ni-Na-FAU series, measured at 50 bar, 160°C and WHSV between 6-2000 h^{-1}.

References: [1] Ehrmaier, A., Liu, Y., Peitz, S., Jentys, A., Chin, C. Y.-H., Sanchez-Sanchez, M., Bermejo-Deval, R. and Lercher J. ACS Catal. 9, 315 (2019).

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Catalytic Properties|Zeolites/Inorganic materials

FEZA21-OR-037

Computational studies on the early stages of the Methanol to Hydrocarbons and related processes

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Abstract Text: We are using state-of-the-art molecular simulations with validation of those results against recent experimental FT-IR, neutron scattering and 2D solid-state NMR studies, to have a better understanding of the factors influencing the early reaction stages and gain a better insight on the ‘hydrocarbon pool’ of the highly important Methanol to Hydrocarbons (MTH) and related processes. Experimental studies shown that methanol can spontaneously convert to methoxy at room temperature.[1] We are employing the QM/MM embedded cluster approach to provide an in depth analysis of the vibrational frequencies of adsorbed the normal and deuterated methanol and methoxy on Brønsted acid sites,[1] validating the observed room temperature methoxylation.

Furthermore, Molecular Dynamics (MD) techniques simulated with CP2K are used to illustrate the methanol environment inside the zeolite pore prior to the initial methoxylation step of the MTH process. The MD simulations are then complemented by Metadynamics simulations to understand the role of methanol loading and acid sites ratio in H-ZMS-5 and highlight the synergistic role of Brønsted acid sites on the methoxylation barrier.[2]

In addition, a separate study conducted on the initial compounds produced from the insertion of CO, ketene and methanol mixture inside different types of zeolites, is presented. 2D solid-state NMR identified different types of intermediates leading to the first C-C bond, depending on the type of zeolite employed. We are using VASP periodic DFT calculations as our computational environment to determine different observables describing sorbate-zeolite interactions in H-ZSM-5, H-ZSM-22, H-MOR and H-FER of several types of intermediates that can be involved in the MTH process as well. [3]

Image 1:

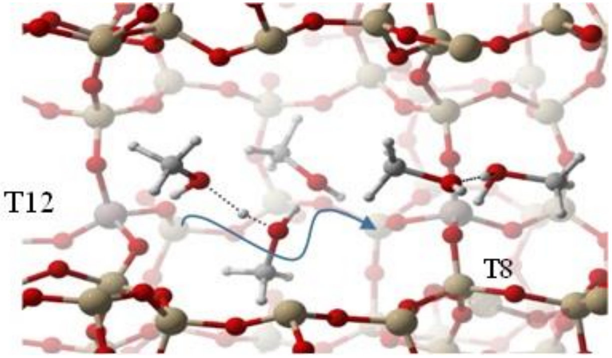
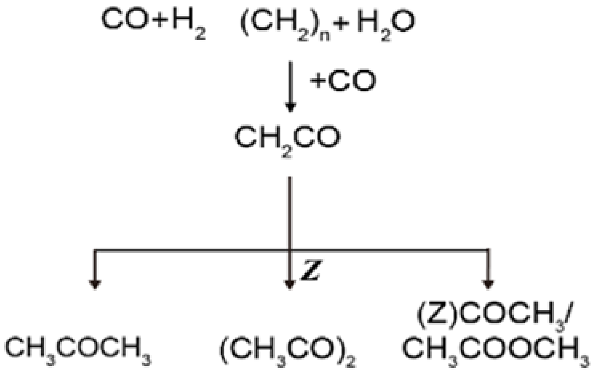


Image 2:



References: (1) Matam, S.K., Nastase, S.A.F., Logsdail, A.J., Richard. A Catlow, C.; Chem. Sci., 2020, 11(26), pp. 6805–6814.
(2) Nastase, S.A.F., Cnudde, P., Vanduyfhuys, L., De Wispelaere, K., Catlow, C.R.A., Logsdail, A.J. ACS Catal., 2020, 10(15), pp. 8904–8915.
(3) Ramirez A., Gong X., Caglayan M., Nastase S.A.F., Abou-Hamade E., Gevers L., Cavallo L., Dutta Chowdhury A., Gascon J., manuscript submitted.

Gas Adsorption, Separation and Storage

FEZA21-OR-038

A Transferable Force Field for Predicting Adsorption and Diffusion of Hydrocarbons and Small Molecules in Silica Zeolites with Coupled Cluster Accuracy

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Abstract Text: As an increasingly valuable complement to experiment, computational modeling approaches such as Grand Canonical Monte Carlo (GCMC) and Molecular Dynamics (MD) have been used to predict adsorption and diffusion properties ahead of experiment for guest molecules in porous materials like zeolites and interpret experimental observations at the molecular level. Successful implementation of GCMC and MD simulations requires reliable force fields (FFs) to describe the interactions of guest molecules with porous frameworks. Developing accurate and transferable FFs for adsorbed and diffused molecules is challenging. Since first-principles quantum mechanical (QM) methods are capable of accurately predicting intermolecular interactions, deriving FFs from QM data without experimental input is a promising solution.

We present a transferable FF for hydrocarbons (linear and branched olefins and paraffins) and small adsorbates (CO_2, O_2, N_2, and H_2O) in pure silica zeolites. The fitting procedure is based on adsorbate–adsorbent interaction energies obtained from periodic density functional theory calculations and corrected using coupled-cluster methods applied to small clusters. The fitting approach aims at accurate prediction of both adsorption and diffusion properties by using sets of configurations that sample adsorption sites and intracrystalline hopping transition states. The quality of the FF is assessed for a wide range of adsorbates in zeolites with different topologies, showing good agreement between theoretical predictions and wide range of experimental measurements of adsorption and diffusion. We also extend this FF to small molecules in alkali metals (e.g., Na, K, Li, Rb, and Cs) exchanged zeolites.

Gas Adsorption, Separation and Storage

FEZA21-OR-039

Variation in water vapor and CO2 adsorption equilibrium on MOFs and Zeolites due to outgassing conditions

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Abstract Text: Crystalline solids with controllable structures possess tailored porosity and large surface areas. This is particularly attractive for gas storage and separation applications. Physisorption of gases is a technique applied for the characterization of porous solids, such as zeolites and metal-organic frameworks (MOFs). Gravimetric vapor sorption and gas adsorption techniques measure promising functionalities such as removal of carbon dioxide (CO_2) from the atmosphere or stability of sorbents in humid environments. Currently, both techniques are routinely applied for characterization of porous solids to explore adsorption capacities and porosity. However, only few studies focus on the pre-experimental conditions for the determination of gas/vapor sorption isotherms. Details of outgassing conditions, despite their importance, are often lacking in research publications. Outgassing at low temperatures of thermally stable material provide an incomplete cleaning of the porous surface. As a result, the ability of sorbents to store CO_2 or water molecules is underestimated based on adsorption data. Contrary, outgassing of temperature sensitive sorbent at elevated temperatures can cause irreversible structural changes which will have profound effects on the adsorption capacities. The impact of water adsorption on the structure was isolated by introducing partial pressures of water under vacuum. Such measurements provided a true water adsorption isotherm without unnecessary interference from a carrier gas. CO_2 adsorption data were measured from low pressures up to 1bar. CO_2 adsorption in the presence of water on the sorbent was collected in a system under vacuum. The results show that the performance of the sorbent can be significantly modified depending on outgassing conditions.

Gas Adsorption, Separation and Storage

FEZA21-OR-040

Assessment of the adsorption step duration and purge flowrate on the performance of demand-driven PSA units

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[1]Department of Chemical Engineering, Vrije Universiteit Brussel, Brussels, Belgium

Abstract Text: **Introduction**

Pressure swing adsorption (PSA) is a well-known gas separation technique with many industrial applications such as hydrogen purification, air drying and biogas upgrading. Generally, PSA units are associated with a high energy efficiency and have a flexible operating range, making them an attractive separation technique [1]. However, designing and optimizing remains time demanding an iterative in nature due to the complexity of the PSA process [1, 2]. In addition, industrial applications may place constraints on certain key performance indicators (KPI's), such as the purity, recovery and productivity. On top of this, seasonal fluctuations can further complexify the design and optimization. Consequently, achieving performant behavior under a wide range of conditions is an additional challenge. Multi-objective optimization algorithms may aide in the search for optimal PSA designs [3]. Unfortunately, the physical understanding of the individual parameter effects may become obscured since typically all the operating parameters are altered simultaneously [4]. On the other hand, parametric studies usually examine individual effects for a single feed or product flowrate. Consequently these studies do not provide equitant information for demand-driven production where the product flowrate varies. Therefore, the aim of this work was to investigate the individual effects of the adsorption step duration and purge flowrate on the performance characteristics of a demand-driven PSA unit where the product flowrate is altered.

Methodology

The effect of adsorption duration and purge flowrate on the performance of a demand-driven PSA were studied using a model for biogas upgrading. The operating parameters were varied individually and examined for a wide range of total productivities. The effects on the performance were considered using three KPI's: purity, recovery and total productivity. The tradeoffs between the KPI's were considered using 3D-graphs. Lastly, the Pareto frontier was visualized using contour plots for a constant productivity and purity constraint.

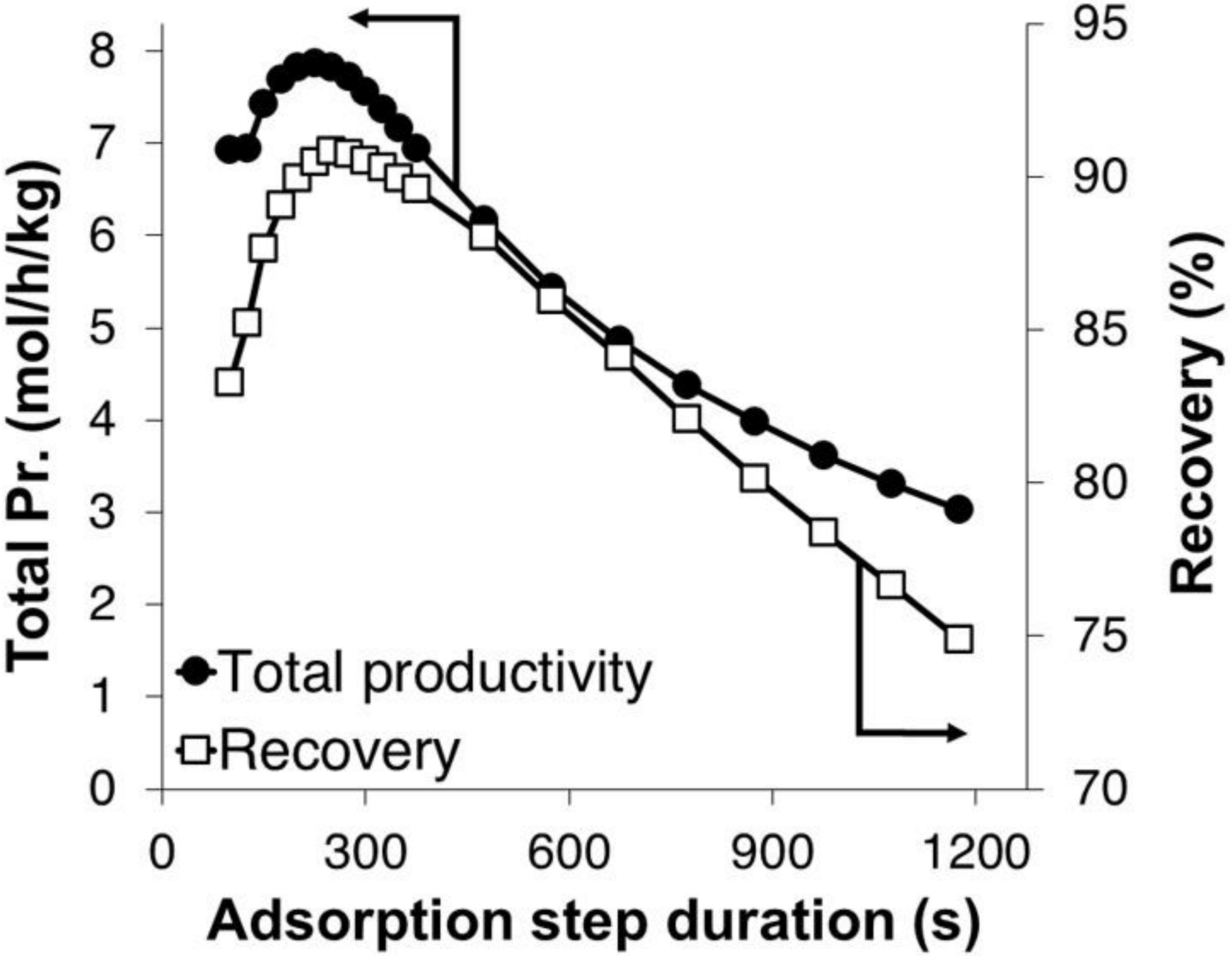
Results and discussion

The adsorption duration and purge flowrate were individually varied and examined for a total productivity range of 2.2 to 10.6 mol/h/kg. Increasing the total productivity led to higher recovery and lower purity. Increasing the purity levels decreased the recovery of the unit. In addition, optimal adsorption durations and purge flowrates at 97% purity were found for each KPI (Figure 1). The recovery and total productivity at 97% purity are maximized at a similar adsorption duration of 225 and 250 s respectively. Above the optimal adsorption duration, the breakthrough of carbon dioxide during the equalization step took place. Below this optimal value, insufficient purging of the column was noticed. The purge flowrate is a tradeoff between high purging to achieve increased total productivities and purities, or conserving purge to increase the recovery.

Figure 1: The total productivity (circles) and recovery (squares) at 97% purity in function of the (left) adsorption step duration and (right) purge flowrate. The arrows indicate the corresponding y-axis of the data.

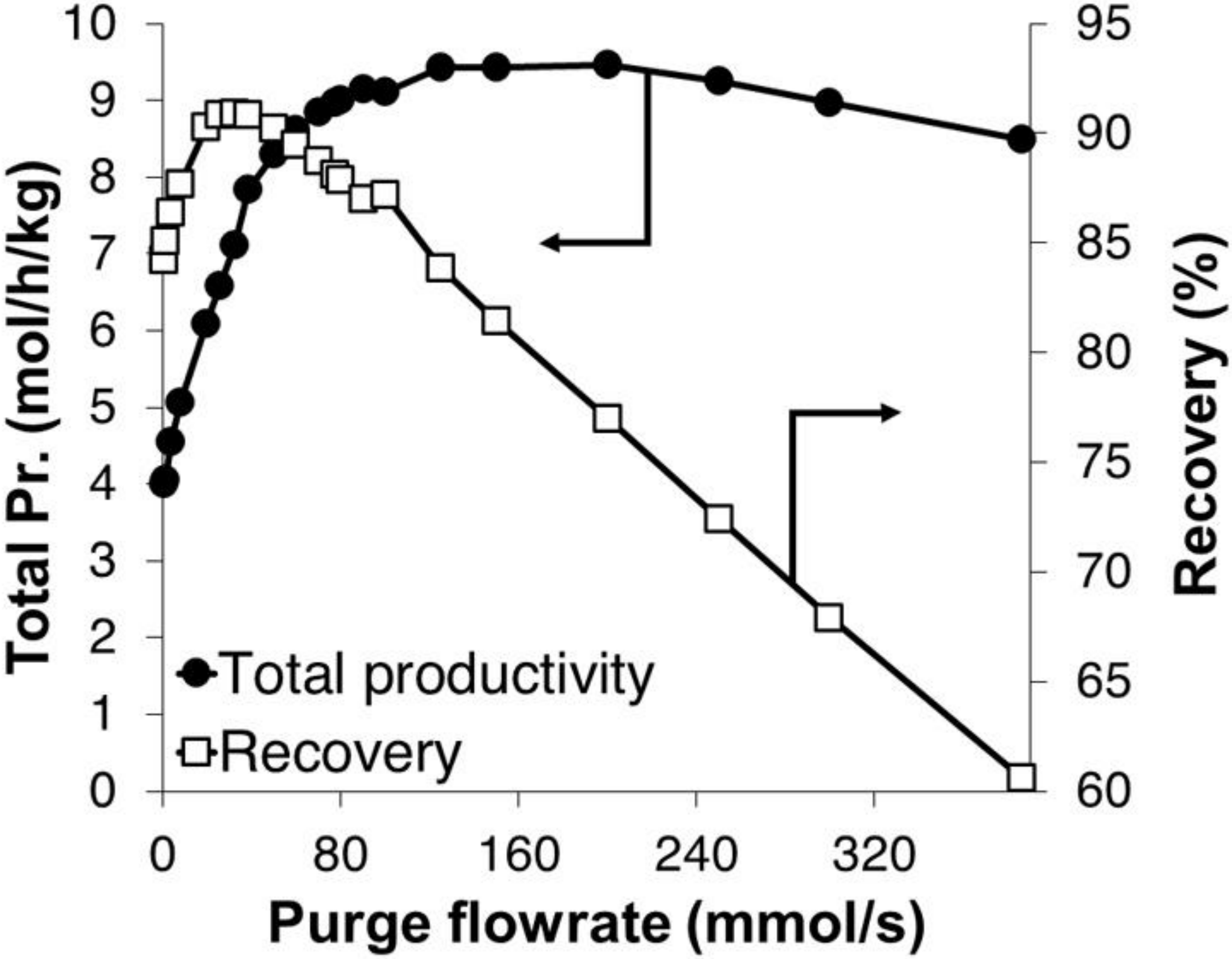
The tradeoffs between KPI's can also be visualized and discussed using Pareto frontiers allowing to identify suitable operation settings for adsorption time and purge flowrate depending on the process requirement. The zone of adsorption durations leading to high recovery and productivity at minimum 97% purity was found to be very narrow. Meanwhile, the performance is less sensitive to the purge flowrate and there is a larger zone between the optimal purge flowrates

Image 1:



Total Pr. (mol/h/kg)
8
7
6
5
4
3
2
1
0
Recovery (%)
95
90
85
80
75
70
0
300
600
900
1200
Adsorption step duration (s)
●Total productivity
□Recovery

Image 2:



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Gas Adsorption, Separation and Storage|Zeolites/Inorganic materials

FEZA21-OR-041

Transition metal cation-exchanged SSZ-13 zeolites for CO2 capture and separation from N2

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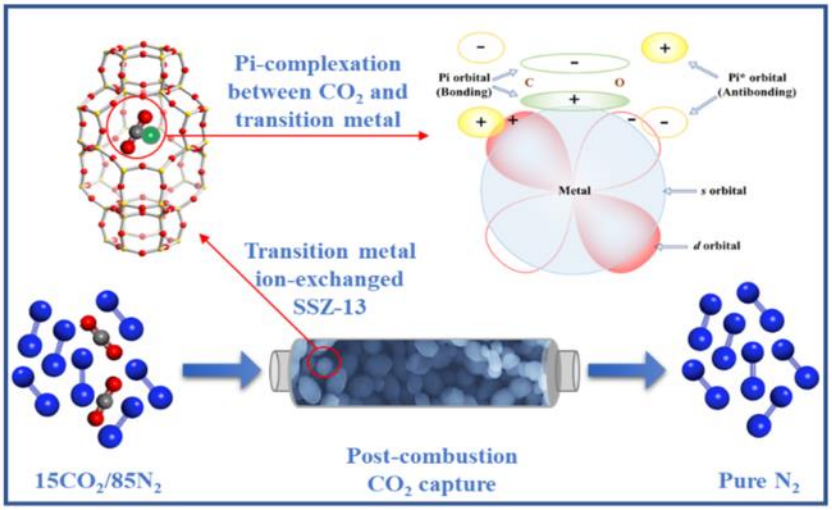
Abstract Text: CO2 capture from post-combustion flue gas mixture (CO2/N2:15/85) is challenging and requires adsorbents with high capacity and high selectivity toward CO2. Our work validated the potential of transition metal cation-exchanged SSZ-13 zeolites for efficient CO2 capture, as evaluated by unary static isothermal adsorption and binary dynamic column breakthrough experiments as well as predicted performance in pressure/vacuum swing adsorption (P/VSA) process. Among the investigated transition metals (Co(II), Ni(II), Zn(II), Fe(III), Cu(II), Ag(I), La(III), and Ce(III)) exchanged SSZ-13, Co(II)/SSZ-13 and Ni(II)/SSZ-13 showed the highest CO2 uptake (4.49 and 4.45 mmol/g, respectively) and superior selectivity of CO2 over N2 (52.55 and 42.61, respectively) at 273 K and 1 atm. We attribute such outstanding separation performance to the Pi backdonation exclusively formed between CO2 and transition metal cation sites. This demonstrates a new approach of developing adsorbents for CO2 capture in the real-world industrial processes.

Image 1:



Gas Adsorption, Separation and Storage|Zeolites/Inorganic materials

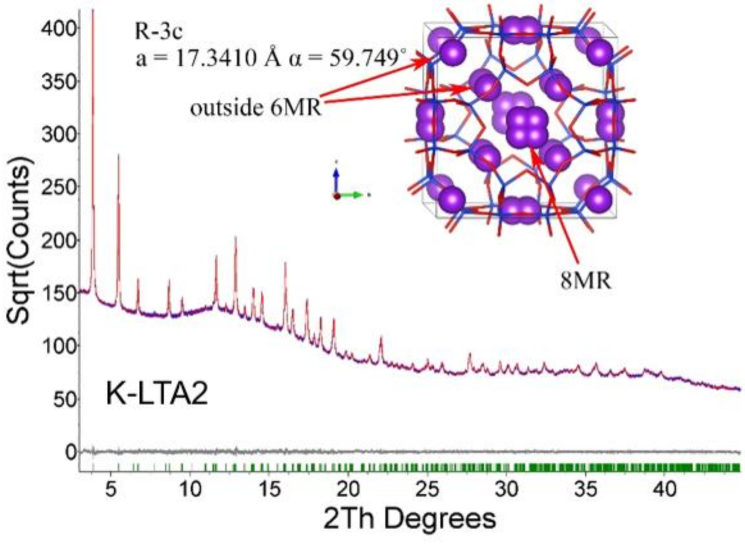
FEZA21-OR-042

Revisit the molecular sieving behaviour in zeolite LTA for high-performance gas separation

J. Shang*

Abstract Text: Chemical separation plays a vital role in the societal development, accounting for 15% annual total energy consumption globally. An efficient alternative technology to conventional distillation would bring huge benefits though reducing energy use, emissions, and pollution. Molecular sieving represents the most desirable approach for separation, where it discriminates molecules by size/shape and exclusively allows for certain component to enter, ideally achieving absolute separation. Zeolite LTA is the most prominent example of molecular sieves. For example, people have been long believing that zeolite 3A (K form) excludes molecules (e.g., CO_2 being 3.3 Å in kinetic diameter) larger than its pore aperture size of 3 Å, while zeolite 4A (Na form) with pore aperture size of 4 Å admits both CO_2 and N_2 (3.64 Å). Prominent researchers in this field have fine-tuned the aperture size by adjusting the relative composition of Na and K to be seemingly between CO_2 and N_2, realizing sieving between these two gases. Despite the exciting separation results, such a size-based sieving may not be the true underlying mechanism. Our recent discovery of molecular trapdoor mechanism in another small-pore zeolite molecular sieves, chabazite, should account for this scenario in LTA. In molecular trapdoor mechanism, different molecules are discriminated based on the ability of guest molecules to temporarily and reversibly move the "door-keeping" cations and thus to enter, rather than size-match. With this in mind, we revisited zeolite LTA and strikingly observed significant CO_2 admission in 3A although the kinetics is relatively slow, which is counterintuitive from the conventional perspective of molecular sieving. We further proved that K-form LTA with reduced cation density (Si/Al = 2 vs. conventional Si/Al = 1) showed consistent results. Establishing the new understanding of non-size based sieving will allow for the developing next-generation molecular sieving adsorbents for highly efficient separation currently not possible.

Image 1:



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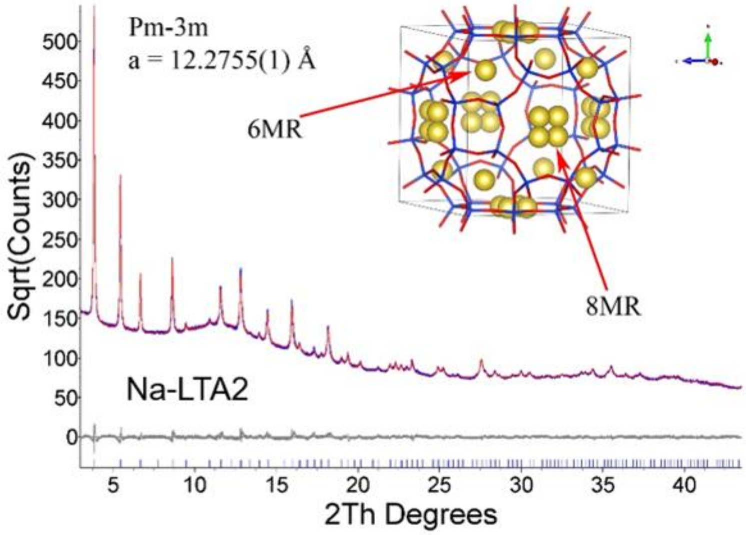

Pm-3m
a = 12.2755(1) Å
6MR
8MR
Na-LTA2
Sqrt(Counts)
0
50
100
150
200
250
300
350
400
450
500
5
10
15
20
25
30
35
40
2Th Degrees

Gas Adsorption, Separation and Storage|Zeolites/Inorganic materials

FEZA21-OR-043

Porous boron nitride - Moving up the scale for use in molecular separations

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Abstract Text: Industrial separation processes account for 10-15% of the global energy consumption[1]. The energy cost of large-scale gas and liquid separation processes (e.g. distillation) could be significantly reduced by moving towards adsorption processes, i.e. using porous materials to separate molecules based on size and/or chemistry. An example of an adsorbent is porous boron nitride (BN): this material exhibits high surface area, high porosity and benefits from greater oxidative and thermal stability than common carbonaceous adsorbents[2]. In this project, we are exploring the potential of porous BN as an efficient and recyclable adsorbent for molecular separations at industrial scale.

Recently, our group developed a new method to produce porous BN with enhanced surface area, tuneable porosity[3] and promising liquid and gas separations performance. To further advance the use of porous BN, we must investigate its chemical stability. In fact, preliminary tests in our group point to the instability of the material in presence of water[4]. Considering this aspect, we functionalised the surface of porous BN via silanisation to enhance hydrophobicity and resistance to moisture. The samples were characterised before and after functionalisation using FTIR, XRD, XPS, TGA and SEM. The changes in hydrophobicity were monitored using water vapour sorption and contact angle measurements. In addition, the porosity of the material was probed before and after exposure to moisture and liquid water with nitrogen sorption. The results point to the efficiency of the approach to produce moisture-resistant BN-based adsorbents.

In parallel, we started investigating the formation mechanism of porous BN via the full characterisation of intermediates at different synthesis temperatures. The results of this study will not only provide valuable insight on how to tune better the porosity of the material, but also on how to improve the hydrolytic stability discussed above. Both the water stability improvement and the BN formation mechanism will be covered in this presentation.

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Gas Adsorption, Separation and Storage|Zeolites/Inorganic materials

FEZA21-OR-044

Use of atomistic simulations and machine learning perturbation theory to design optimized zeolite formulations for selective trapping applications

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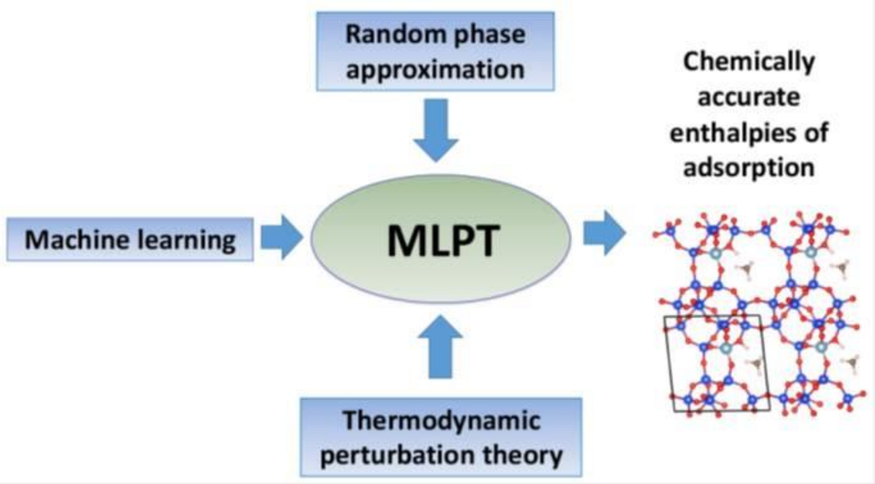
Abstract Text:

Nowadays the degree of sophistication of atomistic simulations based on density functional theory (DFT) can be very high and "numerical experiments" can be realized [1-9]. Combining different atomistic simulation techniques such as ab initio molecular dynamics with advanced method such as many-body schemes to take into account non-local dispersion forces, one can predict adsorption enthalpies of molecules in nanoporous materials. This allows a fast screening of a large number of formulations to design efficient and selective adsorbents with optimized properties for various applications. Taking the example of zeolites, it is now possible to screen several microporous framework structures (e.g. CHA, FER, FAU, MOR, ZSM-5) with various Si/Al ratios [2], and containing various charge compensating cations (alkaline and transition metals) in different oxidation states in a relatively short time [3,4]. The use of atomistic simulations also helps to understand at a molecular level the interactions between molecules and materials. We will give some applications of these modeling tools for the selective capture of radioactive iodine in case of nuclear severe accident [2-5], for the production of biofuels from biomass waste [6,7], or for the development of sensors for Volatile Organic Compounds (lung cancer detection) [8,9].

In an effort to further improve the accuracy of ab initio simulations and reach the chemical accuracy at a moderate computing cost, we also propose a method that couples machine learning techniques with thermodynamic perturbation theory to estimate finite-temperature properties using correlated approximations [10]. We apply this approach to compute the enthalpies of adsorption in zeolites and show that reliable estimates can be obtained by training a machine learning model with few energies computed at the Random Phase Approximation level of theory, which is among the most accurate quantum methods available today for periodic solid state calculations [11]. This approach paves the way to the broader use of computationally expensive quantum-chemical methods to predict the finite-temperature properties of condensed matter systems. In close connection with experiments, this theoretical methodology opens the path to an integrated approach for the development of optimized nanoporous materials and processes in the fields of catalysis and environment.

This work is supported through the COMETE project co-funded by the European Union under the program FEDER-FSE Lorraine et Massif des Vosges 2014-2020.

Image 1:



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Gas Adsorption, Separation and Storage|Zeolites/Inorganic materials

FEZA21-OR-045

Influence of the compensating cation nature on the water adsorption properties of zeolite and their associated composite material forms

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Abstract Text: The control of humidity in food packaging, pharmaceutical and cosmetic products in order to increase their lifetime have attracted more attention in this century by the development of more sophisticated technologies to inhibit the water negative effects on these products. One of the easiest and low cost way to eliminate water molecules is the use of porous materials. Among a variety of porous materials explored (zeolites, metal organic frameworks, clays, carbon based adsorbents, organic polymers), aluminosilicate zeolites with low Si/Al ratio such as LTA and FAU-type zeolites [1, 2] seem to be the most interesting class of materials due to their selectivity and significant adsorption capacities from the low concentration of water in the atmosphere [1]. Unfortunately, synthetic zeolites are generally obtained as powders leading to non-bonded particles. In most applications, zeolites have to be shaped for more convenience (transport, handling...). In our case, it is principally to avoid particulate contamination. The incorporation of zeolite particles directly in the packaging by mixing them to the polymers can be the ideal solution but often the microporosity of the zeolite is partially or totally inaccessible. Hence, formulations and manufacturing methods allowing the conservation of the zeolites adsorption properties after shaping are highly desired.

In this work, LTA-type and FAU-type zeolites were exchanged at a laboratory scale (~ 20 g) and scaled up to 2 Kg using $MgCl_2$ and LiCl aqueous solution. In comparison to the parent samples, the water adsorption capacity increased up to 17% and 28% for the lithium form of LTA and FAU type zeolites, respectively, while for the magnesium forms, an increase of 30% is observed for both zeolites. These trends were conserved when the study was scaled to 2 Kg of exchanged LTA-type zeolite in powder form. Then, theses exchanged zeolites were mixed with polymers to manufacture composite materials containing up to 70% of their weight in zeolites, using extrusion and injection processes. Composite materials containing the LTA-type zeolite exchanged with Mg showed an increase of ~ 20% of the water adsorption capacity in comparison to the parent composite material; meaning that the adsorption properties of the zeolite powders could be conserved after shaping zeolites into composite materials. These composite containing exchanged zeolites with magnesium are promising for technological use due to their excellent mechanical properties avoiding zeolite particles spreading during their use and their higher adsorption performances.

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Gas Adsorption, Separation and Storage|Zeolites/Inorganic materials
FEZA21-OR-046

Tuning CO2 Adsorption of Merlinoite via Cation Exchange

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Abstract Text:

Small pore zeolites of specific structures and compositions have recently been found to show very high selectivity for CO_2 over less polar gases such as CH_4 and N_2. This behaviour was attributed to two mechanisms such as cation gating ("trapdoor" behaviour) and cation-controlled molecular sieving.[1,2] Zeolite Rho is an example of a material, where modification of the pore size via changes in the cation composition can tune the adsorbent properties.[2] In order to optimise kinetics and selectivity, the properties of other flexible zeolites can be tuned via modification of cation content.

Similar to Rho, merlinoite (MER) zeolite, a promising candidate for carbon capture, is a small pore zeolite characterised by a low Si/Al and its 3-D interconnected 8-ring channel system. We recently demonstrated the cation-controlled molecular sieving behaviour of MER zeolite including breathing and CO_2-triggered pore opening.[3] Its monovalent cation forms show different behaviour attributed to the "breathing" transition from narrow to wide pore framework forms as p_{CO2} is increased. The specific uptake of CO_2 decreases with the larger cations and the shape of the adsorption isotherms and the kinetics of adsorption depends strongly on the cation form. In addition, these materials show very low uptakes of CH_4 in single-component adsorption measurements.

The present study shows it is possible to modify 'gate opening' pressure and isotherm shape by modification of the extra-framework cation content. Novel MER material with an elevated Si/Al ratio and its various monovalent cation forms, including Li-MER, has been prepared. Introducing lithium in the merlinoite structure results in adsorption isotherms with very low uptake at low pressures but opening at higher pressures (Image 1). Furthermore, it has been found that the adsorption behaviour can be tuned by ion exchange to prepare mixed cation materials to control the narrow-to-wide pore transition in the 0-5 bar regime.

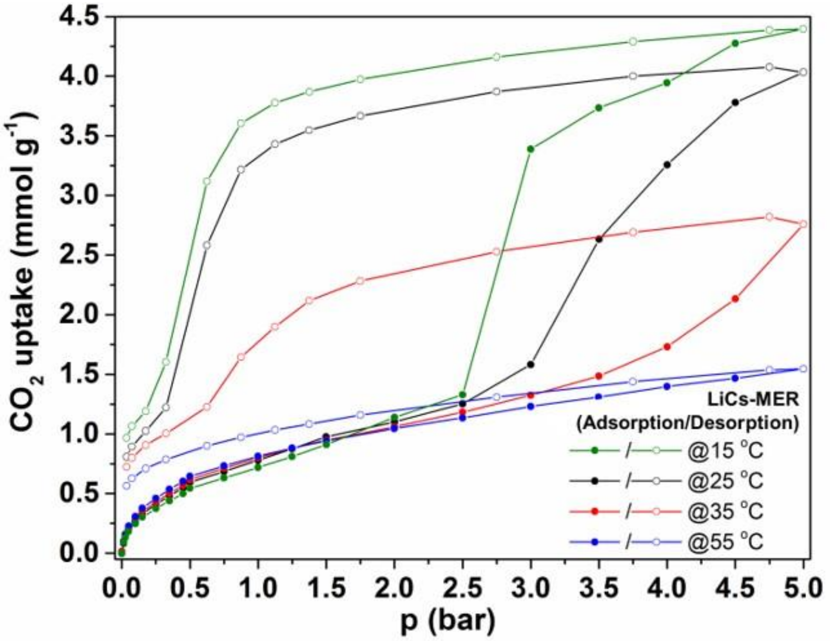
The differing behaviour of the cation forms can be related to structural changes during CO_2 uptake measured by variable-pressure XRD. Combination of in-situ synchrotron XRD and adsorption studies allows a deeper understanding of the structural and gas-adsorption properties of univalent cation forms of the flexible merlinoite zeolite, such as its channel dimension and the location and interaction of cations and gas molecules in the pores.

Acknowledgements

The authors acknowledge the financial support provided by EPSRC (Cation-Controlled Gating for Selective Gas Adsorption over Adaptable Zeolites (EPSRC EP/ N032942 (VG, PAW); EP/N033329/1 (MV, SB)).

Image 1. High-pressure CO_2 adsorption isotherms at different temperature for LiCs-Merlinoite zeolite.

Image 1:



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Gas Adsorption, Separation and Storage|Zeolites/Inorganic materials

FEZA21-OR-048

Measurements of CO2 kinetics in a flexible zeolite using the Zero Length Column method

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Abstract Text: Small pore zeolites, such as those of the Rho family are receiving increasing attention of late, due to their relatively high CO_2 capacity and promising selectivity for CH_4/CO_2 separation. Apart from these characteristics, all members in the Rho family also exhibit some degree of framework flexibility. This is not only apparent in crystallographic studies, but can additionally lead to non-type I isotherms, often involving steps. Such stepped isotherms however, provide a challenge when attempting to measure and model kinetic behaviour of these materials, information which is essential for a material's effective utilisation in industrial separation processes and process simulators. A technique commonly used to measure these characteristics in microporous solids, is the zero length column (ZLC) method. This technique typically involves measuring the desorption of a previously saturated sample after a step change in the gas phase concentration. Kinetic information can be extracted by fitting the experimental data to a theoretical model, in which the relevant molecule's diffusivity through the zeolite structure is a model parameter. Knowledge of the adsorption isotherm is critical in applying this model, but to date the methodology has only been applied to materials exhibiting type I isotherms.

In this study, we employ the recently developed Rigid Adsorbent Lattice Fluid (RALF) to model the CO_2 adsorption isotherm of one the Rho family members, ZSM-25. ZSM-25 exhibits a number of structural changes, including unit cell expansion and cage distortions, upon adsorbing host molecules, such as water and CO_2. Despite its relative simplicity, the RALF model can reflect these structural changes, as observed by *in situ* X-ray diffraction studies, and consequently yield model isotherms which closely resemble the experimentally observed ones (Figure 1). The main advantage of using RALF instead of empirical models are its thermodynamic consistency and applicability over a wide range of process conditions, using a limited set of physically meaningful modelling parameters. This equilibrium model can subsequently be used to simulate the desorption profile of a ZLC experiment, using numerical methods, with a minimum of fitting parameters, allowing to extract kinetic information on this flexible material (Figure 2).

Image 1:

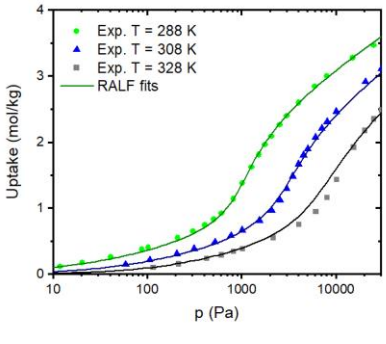
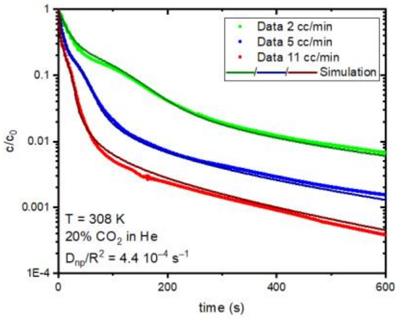


Image 2:


1
0.1
0.01
0.001
1E-4
c/c_0
0
200
400
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time (s)
Data 2 cc/min
Data 5 cc/min
Data 11 cc/min
Simulation
T = 308 K
20% CO_2 in He
$D_{np}/R^2 = 4.4\ 10^{-4}\ s^{-1}$

Gas Adsorption, Separation and Storage|Zeolites/Inorganic materials

FEZA21-OR-050

Binderless zeolite beads with hierarchical porosity for selective CO2 adsorption

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Abstract Text: The concentration of carbon dioxide in the atmosphere is the largest among all anthropogenic greenhouse gases. Some of the largest sources of CO_2 emissions are industrial plants, such as cement and ammonia plants, and thermoelectric power plants[1]. Other common sources that contain large amounts (40-60 vol%) of CO_2 are biogas and landfill gas. The capture of CO_2 from these sources is an important step towards reducing the environmental impact of these processes. An attractive method to separate CO_2 from other gases, such as N_2 (for CO_2 capture from flue gas) or CH_4 (for biogas and landfill gas) is by using solid adsorbents, such as zeolites.

In order to use zeolites in an adsorption process, they must be macroscopically shaped to minimize the pressure drop over the column[2]. Typically, an inert binder material is added to the zeolite powder to form beads or pellets. However, this decreases the adsorption capacity per gram, and high mechanical stability and facile diffusion of CO_2 into the pores can be a tradeoff. In this research, we investigate an attractive alternative: binderless zeolite beads with hierarchical porosity. These novel zeolite beads were prepared using Amberlite resin beads as a hard template, as depicted in Image 1.

Our results show that the crystallinity of the zeolite beads has a large effect on the CO_2 adsorption capacity; when XRD measurements show that the zeolite is partly amorphous, the adsorption capacity is significantly lower than when no amorphous parts are detected by XRD. The adsorption capacity of our zeolite A beads is 3.6 mmol/g at 1 bar, which is similar to commercial zeolite A beads (see Image 2), and comparable to zeolite A powders reported in literature. Post-synthesis modification of our beads by ion-exchange can further increase the selectivity towards CO_2, causing our beads to out-perform the commercial beads.

Image 1:

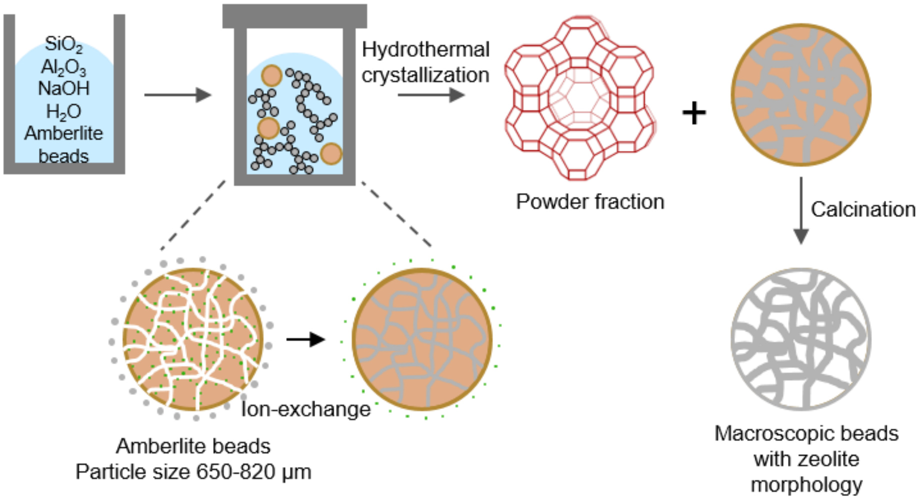
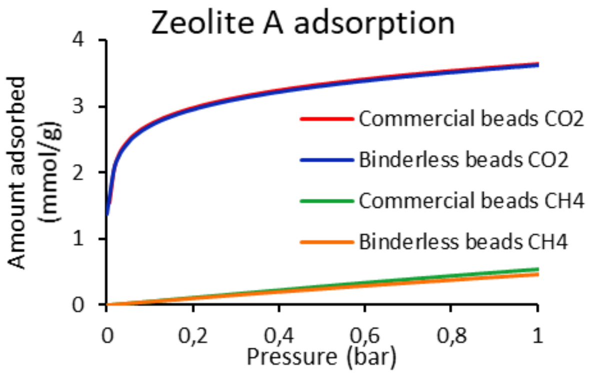


Image 2:



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Ion Exchange and Other Applications

FEZA21-OR-051

A nuclear clean-up act - microporous silicates for decontamination of radioactive waste streams

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Abstract Text: Nuclear power contributes 21% of the electricity generated in the UK,[1] however one of the major challenges facing it is the decontamination and disposal of radioactive waste. There is a particular focus on legacy waste, which was produced during the infancy of the UK's civil nuclear program in the 50s and 60s where long-term waste management was neglected. Most of the medium-lived radioactivity in spent nuclear fuel is produced from Cs-137 and Sr-90, which require removal from aqueous waste streams that can vary widely in pH and contain a wealth of highly concentrated competing cations. Zeolites are widely used to capture radionuclides as their well-known ion exchange properties present a selective, facile, reliable, and cost-effective remediation approach. By immobilising these radionuclides in a solid phase, the waste volume is vastly reduced, and it lowers the risk of these highly soluble cations from leaching into the environment.[2]

Currently, the natural zeolite clinoptilolite is used in the UK nuclear industry to remove Cs-137 and Sr-90 cations from radioactive waste streams.[3] However, clinoptilolite is a finite natural resource and the need for waste decontamination will extend beyond the available supply. We have looked at a group of promising successor materials called umbites, a class of zeolitic microporous silicates. Structurally, the framework consists of oxygen-bridged $[SiO_4]^{4-}$ tetrahedra and $[MO_6]^{8-}$ octahedra, with cation exchange sites occupying the 6-ring and 8-ring channels, as shown in figure 1. The octahedral site M corresponds to a +4 oxidation state metal such as Ti, Zr, Sn or Hf. Doping the M site with a pentavalent metal is seen to enhance the uptake of Cs and Sr.

We report that these doped umbite materials demonstrate sustained Cs removal from solutions containing greater concentrations of common competitor cations such as Na, K, Mg and Ca. This behaviour is also maintained in acidic and basic solutions (figure 2), which are often problematic for zeolites due to structural breakdown. The kinetics of Cs uptake are significantly faster compared to clinoptilolite that is currently used by the nuclear industry, particularly in the presence of competitor cations. In addition, we have investigated improved synthetic approaches that are more suitable for large-scale industrial production. This includes reduced temperature and time, as well as implementing microwave heating techniques. Lastly, we have researched how these materials can best be deployed in industry, such as producing bound pellets and considering potential waste forms that can be used for safe disposal.

Image 1:

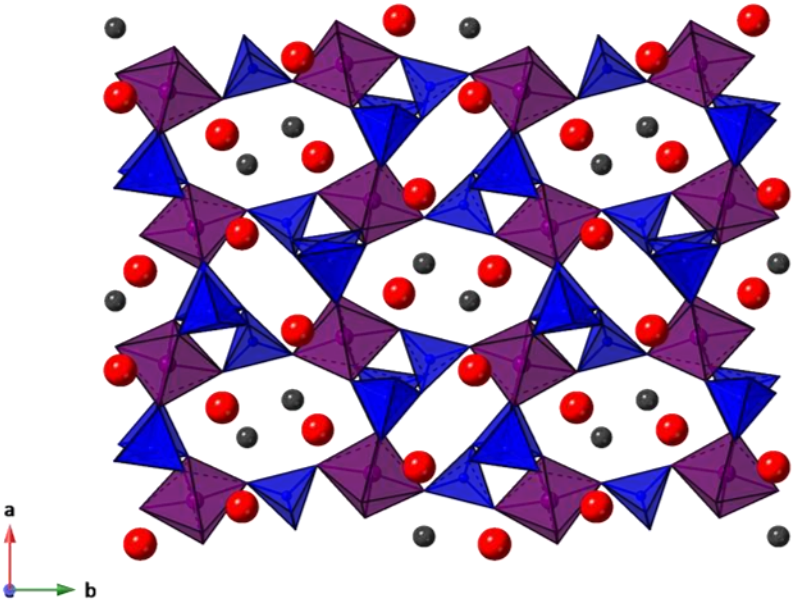
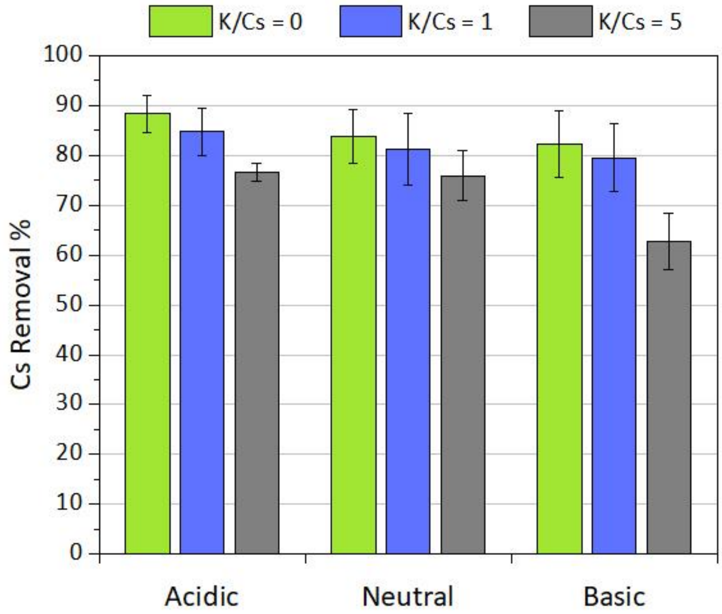


Image 2:



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Ion Exchange and Other Applications

FEZA21-OR-052

Structural studies of titanium and zirconium silicate ion-exchange materials for the treatment of nuclear waste.

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Abstract Text: Zeolites are commonly used as ion-exchange materials for the remediation of nuclear waste; however, they have certain drawbacks. Unlike zeolites which contain SiO_4 and AlO_4 tetrahedra, microporous Ti-silicates can contain SiO_4 tetrahedra and TiO_6 octahedra and therefore structures are possible which have no traditional aluminosilicate analogues [1]. Microporous Ti-silicates such as sitinakite $KNa_2Ti_4Si_2O_{13}(OH)\cdot 4H_2O$ and the synthetic niobium doped analogue are used for the removal of Cs^+ and Sr^{2+} from nuclear waste [2,3]. The work presented here will focus on the structures and thermal behaviour of the ion-exchanged Ti- and Zr-silicates. A clear understanding of both is fundamental in determining if these materials have potential as ion-exchangers within the nuclear industry.

Umbite is a naturally occurring small pore microporous Zr- silicate, found in northern Russia and synthetic analogues, $K_2ZrSi_3O_9\cdot H_2O$, can be prepared in the laboratory [4, 5]. Ion-exchange studies here have shown that umbite has a preference for common radionuclides, such as Cs^+ and Sr^{2+} and Ce^{4+} (as a surrogate for Pu), even in the presence of competing ions. In-situ studies show that these materials behave differently with temperature, indicating that the nature and location of the charge balancing cation plays an important part in determining which high temperature phases are formed and the phases formed do not fit previously reported structures.

Natisite is another material which has interesting ion-exchange chemistry and is a layered Ti-silicate with the formula Na_2TiSiO_5 [6]. The structure consists of square pyramidal titanium, with the sodium cations located between the layers. This coordination environment is highly unusual for Ti. Inclusion of zirconium or vanadium in the framework has a considerable effect on the ion-exchange properties, with changes in the exchange capacity and the rate of uptake for certain ions of interest.

A combination of techniques to probe long and short-range order have been used to understand the ion-exchange behaviour of these materials.

Image 1:

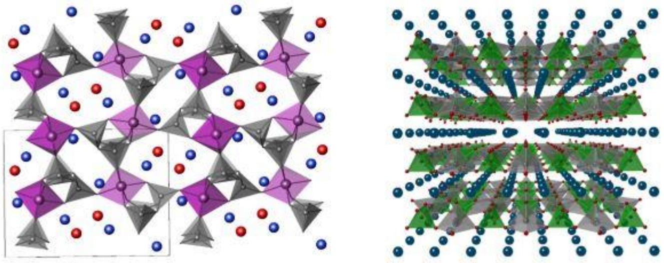

Figure: Structural representation of umbite (right) and natisite (left).

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Ion Exchange and Other Applications

FEZA21-OR-053

Ag-exchanged FAU-type zeolite for the removal of perfluoroalkyl substances (PFAS) from water: a combined in situ synchrotron X-ray diffraction and thermal analysis/isotope ratio mass spectrometry study.

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[1]Department of Physics and Earth Sciences, University of Ferrara, Via Saragat 1, I-44121, Ferrara, [2]Materials Characterisation By X-ray diffraction (MCX) Beamline, Elettra-Sincrotrone Trieste S.C.p.A., Strada Statale 14 - km 163,5 in AREA Science Park, Basovizza, Trieste, Italy

Abstract Text: In recent years, the occurrence and fate of perfluoroalkyl substances (PFAS) in the aquatic environment was recognized as one of the emerging issues in environmental chemistry. In particular, PFOA (C8HF15O2) and PFOS (C8HF17O3S) have recently become the targets of global concern due to their ubiquitous presence in the environment, persistence, and bioaccumulative properties. Strong carbon-fluorine (C–F) bonds make PFOA and PFOS extremely resistant to chemical, thermal and biological degradation, consequently, their removal from water is a crucial scientific and social challenge [1-2]. This work aims to investigate, for the first time, the structural modifications and the desorption kinetics during the thermal activation of FAU and Ag-exchanged FAU-type zeolites used for removal of PFOA and PFOS from water. The introduction of Ag in the framework confers them unique physical, chemical, and antibacterial properties along with strong absorption property, good stability and catalytic activity [3]. In situ high-temperature synchrotron X-ray powder diffraction and thermal analysis coupled with Elemental Analyzer – Isotope Ratio Mass Spectrometry (EA-IRMS) provided to: i) investigate high temperature structural modifications experienced after during PFOA and PFOS thermal desorption and to check the crystallinity preservation of the porous matrix; ii) monitor and evaluate the organics decomposition process upon heating; iii) estimate the influence of Ag active sites in working zeolites; iv) verify the best regeneration temperature in order to verify whether they can be re-used for PFAS removal from wastewater. This information was crucial for designing and optimizing the regeneration treatment of such zeolites, which are revealed to be highly effective in water-remediation technology. Powder diffraction data of each sample were collected at the synchrotron MCX beamline (Elettra, Trieste, Italy) and were subjected to the same heat treatment profile encompassing the heating ramp with a rate of 5°C/min from room temperature to 900 °C. The powder samples were loaded and packed into a 0.5 mm quartz capillary open at one end and heated in situ using a hot air stream. The analysis of the patterns collected using in situ synchrotron XRPD on both as-synthesized and Ag-exchanged Y zeolites showed no heat-induced symmetry change. Moreover, to carry out a comparison, structural data relating to bare zeolites are also reported in order to check the contribution of the loaded organic molecules. The differential thermal analysis (DTA) curve shows two DTA exothermic events between 300 and 600 ºC due to the PFAs degradation, in very good agreement with the EA-IRMS analyses. The complete thermal regeneration of all selected materials was achieved at ~650 °C. No relevant variations were observed in Ag-exchanged materials. This information is crucial to examine the efficiency of Ag-exchanged zeolites compared to same samples taken separately for the adsorption of PFOS and PFOA from water. The diffraction peaks were also accurately monitored to study in real-time their evolution (in terms of broadening, shift, changes of intensities) compared with the Y zeolites without any treatment, after silver activation and as well as after PFOS and PFOA adsorption. The XRD analysis demonstrated that the adsorption/desorption process occurred without significant loss of zeolite crystallinity, but with slight deformations in the channel apertures. The regenerated zeolites regain the unit-cell parameters of the bare materials almost perfectly, however. Only a slight memory effect in terms of structural deformations is registered in channel geometry thus demonstrating that the regenerated samples which could be able to re-adsorb similar amounts of PFOS.

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Ion Exchange and Other Applications|Zeolites/Inorganic materials

FEZA21-OR-054

Oligomerization of Acetylene to Unsaturated C4 Compounds under Pressurized Conditions

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Abstract Text: Oligomerization of Acetylene to Unsaturated C_4 Compounds under Pressurized Conditions

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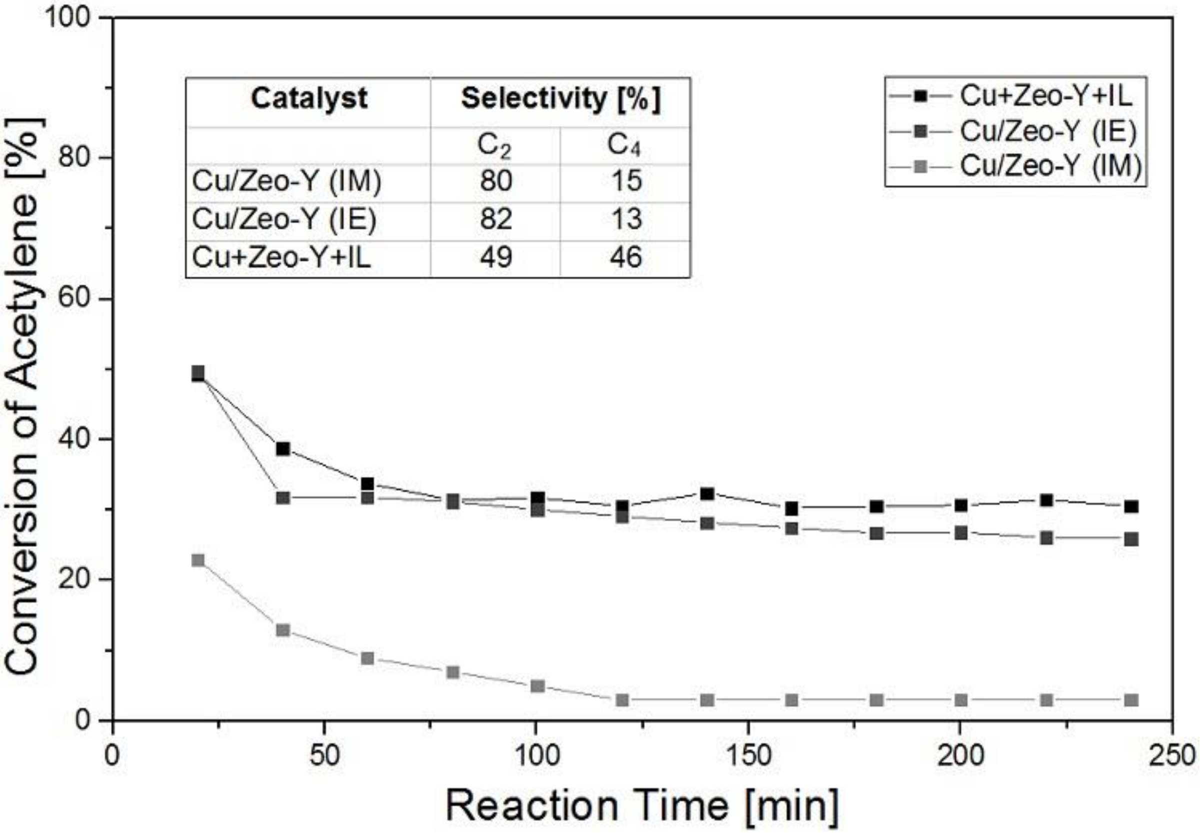
Acetylene was the main feedstock of the chemical industry in the first half of the last century, due to its high reactivity that resulted in a rich chemistry with many applications, including production of acetaldehyde, vinyl chloride, and acrylonitrile. However, after the 1950s, it lost its competitive position to mainly ethylene and propylene, since coal chemistry had started to be replaced by petrochemistry. Moreover, all acetylene production processes require high amounts of energy. Nevertheless, acetylene might become competitive again with naphtha-derived ethylene and other olefins for several reasons including making use of increasing amounts of fluctuating power in the electricity grid from wind and solar energy, an increase in oil prices, and availability of coal as well as natural gas [1, 2]. With this vision, a fully remote-controlled, automated flow reactor system was constructed for acetylene conversion reactions, both batch and continuous flow reactors which allow safe handling of acetylene up to 30 bars. This project offers novel catalytic systems for the selective oligomerization of acetylene under pressure into more valuable products such as butadiene or other unsaturated C_4 products. These products are important building blocks for synthetic polymers, long-chain alcohols and other chemicals. Previous studies from our group revealed Cu/Zeo-Y as a promising catalyst for this reaction. The goal of this study is to further increase the selectivity towards C_4 products, preferably towards butadiene at improved lifetime of the catalyst. During the catalyst screening, the conversion of acetylene (after 20 min) was very low because of very fast deactivation of the solid catalysts. Thus, ionic liquids (IL) were used to prepare Cu/Zeo-Y coated with a thin IL layer in order to avoid, or slow down, catalyst deactivation, which could occur due to production of higher oligomers in the catalyst bed [3, 4].

The conversion of acetylene over the reaction time is shown in Image 1 for three different catalysts. It includes a table that lists the selectivity values towards C_2 and C_4 products as well. As can be seen in the figure, an improvement in both conversion and selectivity towards C_4 product was successfully achieved by testing different catalysts and preparation methods. More specifically, ion-exchanged copper in zeolite pores enhanced the conversion of the acetylene and the stability was improved too. However, the selectivity towards C_4 remained constant at 13%. Nevertheless, addition of IL to this improved catalyst system made a significant change, i.e., a threefold increase in selectivity. Besides, about 30% of the C_4 concentration was 1, 3-butadiene and the catalyst had longer lifetime.

The previously encountered deactivation problem of Cu-based catalysts were solved by the new design of the catalyst system, i.e., confining the copper in the pores of zeolites in cationic form and lowering the reaction rate by an IL layer. The IL has different solubility for acetylene and ethylene [4]. The problem of stability of the catalysts was solved as well.

Image 1: Conversion of acetylene vs the reaction time for different catalyst systems, prepared by impregnation (IM), ion-exchange (IE) and impregnation of copper with Zeo-Y with the addition of IL. For every reaction 200 mg of sieved catalyst (200-300 µm) was diluted with SiC and packed in a quartz reactor. The reaction conditions were 220°C, 10 bar, using a feed stream of C_2H_2:H_2 (1:4) as well as N_2 for dilution, total flow rate being 210 mL/min.

Image 1:



Catalyst	Selectivity [%]	
	C_2	C_4
Cu/Zeo-Y (IM)	80	15
Cu/Zeo-Y (IE)	82	13
Cu+Zeo-Y+IL	49	46

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Ion Exchange and Other Applications|Zeolites/Inorganic materials

FEZA21-OR-055

The unique effect of copper cations on the flexibility of zeolite Rho causes exsolution

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Abstract Text:

We report the unusual structural behavior of the zeolite Cu,Na-Rho upon dehydration. We show that the presence of extra-framework Cu^{2+} cations in the Na-Rho structure results in exsolution behavior, rarely observed for zeolites.

Introduction

Extra-framework cations can occupy three sites in zeolite Rho: double 8 ring (*d*8*r*), single 8 ring (*s*8*r*) and single 6 ring (*s*6*r*) (Figure 1a), and their type and concentration determine its structure and adsorption properties. The flexibility of the Rho framework is remarkable: typically, upon dehydration of its cation forms the unit cell shrinks, and its framework distorts to a lower symmetry form, from $Im\text{-}3m$ ($a \geq 15$ Å) to $I\text{-}43m$ ($a < 15$ Å) (Figure 1a). Until now this behaviour has been observed for all univalent and divalent cations exchanged into zeolite Rho.[1–3] Upon preparation and analysis of the Cu,H-Rho and Cu,Na-Rho series it was observed that Cu^{2+} cations have an unusual effect on the unit cell which no longer distorts upon dehydration and the presence of Na^+ cations causes exsolution into two phases, a Cu-rich phase ($a = 15$ Å) and a Na-rich phase ($a = 14.5$ Å). The coexistence of two zeolite phases is rarely seen, although it has been observed for a specific ratio of K/Na in the flexible zeolite amicite.[4]

Experimental

Zeolite Rho was synthesised according to a reported procedure[5] and converted to Cu,H- and Cu,Na-Rho series by calcination followed by ion exchange. Synchrotron PXRD of the dehydrated samples were obtained and the structures determined by Rietveld refinement. Electron paramagnetic resonance (EPR) spectroscopy was conducted on dehydrated Cu,H-Rho samples.

Results and Discussion

Laboratory XRD indicates that the hydrated forms of all Rho zeolites exhibited $Im\text{-}3m$ symmetry ($a = 15$ Å). Rietveld refinement of Cu,H-Rho samples revealed that their structure did not distort upon dehydration and the unit cell parameter remained *ca*. 15 Å. The cations were located in *s*6*r* and *s*8*r* sites (Figure 1b) and this was further analysed by EPR spectroscopy (Figure 1c).[6]

The synchrotron PXRD patterns of dehydrated Cu,Na-Rho samples with 1 and 4 Cu^{2+} cations per unit cell showed one set of diffraction peaks. However, a splitting was observed for samples with between 2 to 3 Cu^{2+} cations (Figure 1d). The two-phase Rietveld refinement confirmed that the structure of one had a unit cell parameter similar to that seen in the Cu,H-Rho samples , $a = 15$ Å, therefore it was assigned as Cu-rich phase. By contrast, the second Rho phase had a much smaller unit cell parameter, $a = 14.5$ Å, and can be assigned as the Na-rich phase. It appears that, during dehydration, exsolution occurs which results in the formation of the two-phase microstructure.

Figure 1*. (a) Two symmetries of zeolite Rho and cation sites, (b) structure of the Cu_3,H-Rho sample with the location of copper cations, (c) EPR spectra of dehydrated Cu,H-Rho and (d) PXRD patterns of dehydrated Cu,Na-Rho.*

A mechanism of exsolution is suggested, which assumes that in hydrated samples cations can move freely through the structure and upon dehydration, cations diffuse to locate themselves in favourable positions. If the framework was only in the 'open' $Im\text{-}3m$ symmetry, then the Cu^{2+} cations would be well coordinated with a low energy configuration whereas the Na^+ cations would not, while the situation is the reverse for the $I\text{-}43m$ structure. The structural solution, which minimises the energy, is for two phases to form, with consequences for the CO_2 adsorption properties.

Conclusions

The Rietveld refinements on Cu,H-Rho samples showed copper to have a unique effect on the flexibility of Rho framework, not seen before for other univalent or divalent extra framework cations. In a specific range of Cu/Na ratios in Cu,Na-Rho zeolite, it is favourable energetically to have a combination of both framework symmetries as opposed to a single phase and exsolution is observed.

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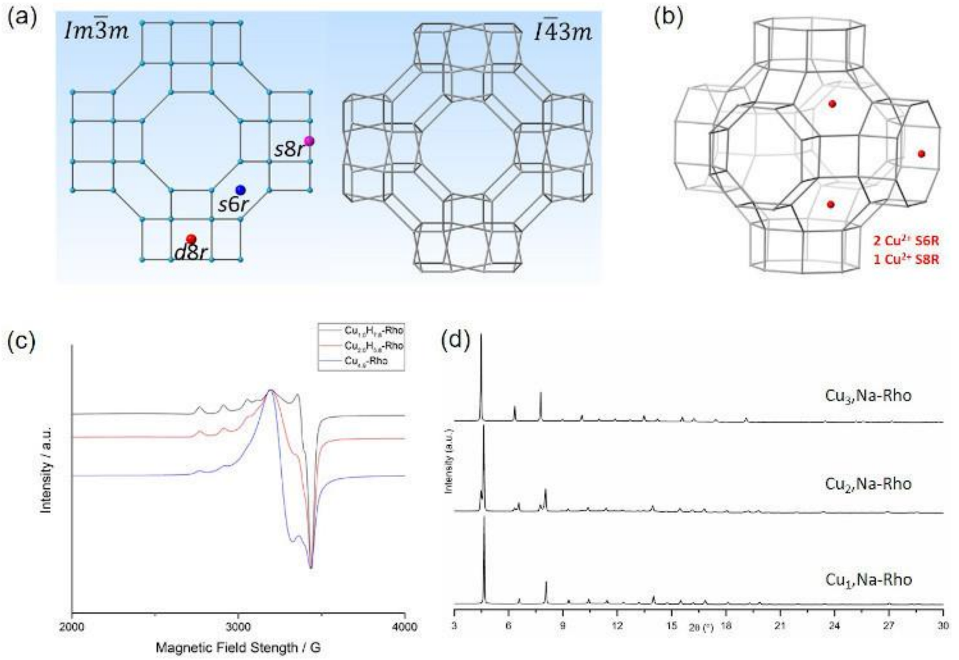
Image 1:



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Ion Exchange and Other Applications|Zeolites/Inorganic materials

FEZA21-OR-056

The ion-exchange mechanism of catalytic transition metals into H-CHA

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Abstract Text: The aluminosilicate zeolite CHA contains Al defects in the tetravalent T-atom positions in the framework that results in a negative charge being imparted onto the zeolite. During the synthesis, these defects are charge-compensated by either cationic structural directing agents[1,2] or alkali metals.[3] However, these original ions do not have any catalytic activity and thus they are ion-exchanged (IE) to form the desired catalyst. A notably example is the commercially relevant NOx abating Cu-CHA catalyst where IE can be performed through: (i) solution IE,[4–6] (ii) incipient wetness impregnation,[7,8] or (iii) solid-state IE.[9–11] A plethora of differing metals species with varying selectivities and catalytic effectivenesses can be deposited depending on the method used and the Si/Al ratio. Despite the ubiquity of these IE procedures and wide-spread application of Cu-CHA, the complete mechanism for ion-exchange is not known and therefore controlling the disposition of these species and catalysis optimisation is not possible. Thus, computational modelling using *ab initio* methods supported by experimental work of this process has been performed in order to determine the IE mechanism for various transition metals with a particular emphasis on Cu(II) and Co(II).

For the solvated migration within the bulk crystal, the rate limiting process is the passage between the CHA cages through the 8-membered rings (8MR) where a meta-stable framework coordinated structure exists as a local minima for the Cu(II) and Co(II) in the plane of the 8MR but for not others. The energy profile of the inter-cage migration is governed by the metal's local geometry and particularly their coordination geometry with the relative position and character of the ligands determining the internal energy. IE fundamentally involves the transport of metal from the exterior of the zeolite to the interior and ergo is critically dependent on the interaction between the metal reagent and the external surface. Given this, models have been expanded to generate exhaustive migration profiles of Cu(II) and Co(II) from in solution to impregnating the CHA crystal in a collection of novel calculations on a previously unreported area. Furthermore, complementary experimental work has been performed to support and valid the computational models. Calculations demonstrate that whilst Cu(II) has a thermodynamic drive to adhere to the predominantly siliceous surface, Co(II) does not with experimental data demonstrating that, unlike Cu(II), a lack of Co(II) below a certain reagent concentration will result in no uptake. Further work undertaken from this study aims to aid in the development of IE methods in order to enable further control over the catalytic metal speciation and thus enable further optimisations.

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Ion Exchange and Other Applications|Zeolites/Inorganic materials

FEZA21-OR-057

Ion-selective pencil: towards a zeolite-based multi-sensor system for precision agriculture

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Abstract Text: 1. Introduction

Development of information technology allowed interconnection of physical sensing devices and their distant monitoring and control over the internet. From remotely operated sensors mainly physical information is gathered, while the chemical information is typically inferred from a range of physical sensors (position, vibration, temperature, humidity). Despite significant recent advances, chemical sensors still require relatively complex handling protocols (storage, calibration, cleaning), which drive their price beyond the possibility to be routinely used in agriculture and projects like Citizen Science. In this work, we are demonstrating the concept of an ion-selective pencil (ISP), a zeolite-based sensor. A user can take the ISP selective for the desired ion, draw a line onto a suitable substrate by mechanical abrasion and connect thus prepared sensors to a readout device that exists in many, if not all homes. In terms of sensing principles, the ISP is analogous to ion-selective electrodes (ISEs). The potentiometric response is characterized by Nernstian equation, with the roles of ISP's components being analogous to their counterparts in ISEs, where conductive polymers (CP) are typically used as the intermediate layer, [1] while carbon nanotubes have also been reported. [2] We have recently demonstrated that simple graphite can also be used as an intermediate layer [3] and a matrix for embedding ionophores. The aim of this work is to demonstrate that zeolites in ISPs can be utilised instead of the traditional ionophores for water and soil analysis.

2. Experimental

A mixture of a zeolite (BEA, FAU, FER, HEU, LTA, LTL, MFI or MOR; Si/Al= 1-40) and graphite powder (<20 µm, Aldrich) in a variety of ratios was homogenized in a mortar, then the mixture was pressed in a pellet by the hydraulic press. Subsequently, a 1.5 cm x 3.0 cm strip was cut from a PET sheet and etched with aluminium oxide (grit 240) for 30 s to increase the adsorption surface. On the etched PET sheet, with the pressed pellet a line was drawn by hand. (Figure 1) As-prepared electrodes were connected to a potentiometer (EMF 16 interface, Lawson Labs, Inc.) via the top end, while the bottom end was submerged in the deionized water. Water was then spiked with 20, 100, 1000 and 10000 µL of 0.1 M chloride solutions of Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}, H^+, Fe^{3+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+} and the potentiometric response was measured.

3. Results and Discussion

Electrode composition was optimised using NaX and graphite. From a variety of zeolite/graphite ratios, 40/60 wt. % exhibited the highest near-Nernstian response to Na^+ (55.1 mV/decade) and a dynamic range between 10^{-5} and 10^{-1} M (Figure 2). The data array has been analysed using statistical methods, demonstrating that a multisensory setup utilising this database of responses as reference values could be applied to determine the unknown concentration of the ions of interest. The overall resistance of ISP is in the order of kΩ, instead of MΩ for typical CP-based ISE, thus requiring less sophisticated readout systems. Since its input impedance is about 1000 times higher than the resistance of ISP, it should be sufficient to suppress sensor polarization.

4. Conclusions

Zeolites offer suitable chemical functionality for the preparation of ISP that can be used with little or no sample preparation, while graphite as a matrix offers ion-to-electron conductivity and sufficiently low resistance so that less sophisticated readout instrumentation can be used than required by its counterpart polymer membrane-based ISE. Simple preparation, handling and measuring protocols, as well as the low cost, offer the possibility that ISP are integrated into large scale sensor networks or Citizen Science projects.

Image 1:

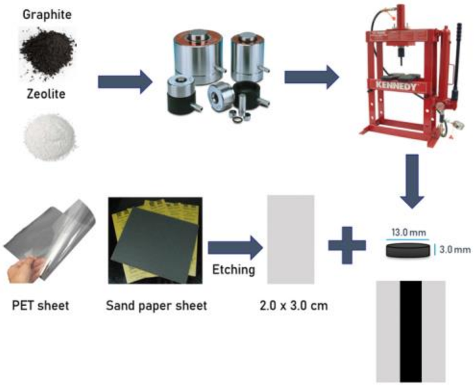
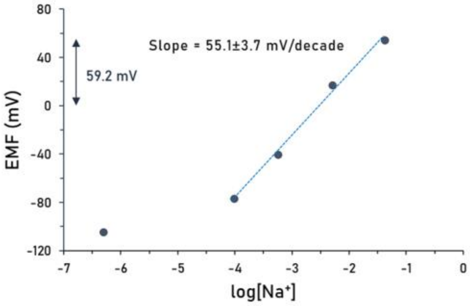


Image 2:



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Ion Exchange and Other Applications|Zeolites/Inorganic materials

FEZA21-OR-058

Design of effective zeolite-based ion-exchangers for radioactive Cs+ and Sr2+ capture

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Abstract Text: Zeolites are widely used as an ion-exchanger for capturing radioactive Cs^+ and Sr^{2+} due to their commercial availability, low material cost, and structural diversity. Unfortunately, important structural factors determining their performance have not been clearly elucidated. To investigate the structure-property relationship, here we prepared thirteen zeolites with various structures and Si/Al ratios [1]. Extensive ion-exchange experiments revealed that Cs^+ exhibited an enhanced affinity to zeolites with high Si/Al ratios, which could be explained by the dielectric theory. Notably, zeolites containing 8-membered ring (8MR) showed outstanding Cs^+ selectivity. Structural analysis using X-ray diffraction proved that Cs^+ with an ionic diameter of 3.6 Å was selectively coordinated within 8MR having a cavity diameter of 3.6–4.1 Å. Such unique “size-selective” Cs^+ coordination seems to be analogous to the ion complexation by macrocyclic organic ligands, such as crown ethers. Divalent Sr^{2+} showed decreasing affinity to zeolites as the Si/Al ratio increased, because of the increasing average Al–Al distance distribution. Sr^{2+} exchange exhibited an insignificant dependence on zeolite structures due to its strong hydration, which inhibited effective interaction with the zeolite frameworks. In terms of kinetics, Sr^{2+} exchange was significantly slower than Cs^+ exchange because of the bulkiness of hydrated Sr^{2+} ions.

We also developed a simple but powerful strategy to generally increase the Cs^+ selectivity of various zeolites. We found that encapsulation of elemental sulfur in the micropores of zeolites via vacuum sublimation can remarkably increase the selectivity toward Cs^+ in the presence of competing ions [2]. Elemental sulfur does not provide additional adsorption sites for Cs^+ ions but increases the ion-exchange selectivity toward Cs^+ by providing additional interaction. Rigorous analyses showed that sulfur partially donated its electron to the ion-exchanged Cs^+ cations in zeolites, indicating significant Lewis acid–base interactions. According to the hard soft acid base (HSAB) theory, the enhanced Cs^+ ion-exchange selectivity could be explained by the fact that sulfur, a soft Lewis base, interacts more strongly with Cs^+, which is a softer Lewis acid than other alkali and alkaline earth metal cations. Because of the high intrinsic Cs^+ selectivity of bare zeolites and selectivity enhancement due to sulfur encapsulation, the sulfur-modified chabazite and mordenite showed the most promising Cs^+ capture ability in the presence of various competing ions. Unfortunately, such sulfur encapsulation did not enhance the zeolites` ion-exchange selectivity toward Sr^{2+}, which could be attributed to the strong hydration of Sr2+ inhibiting the interaction between Sr^{2+} and sulfur.

Image 1:

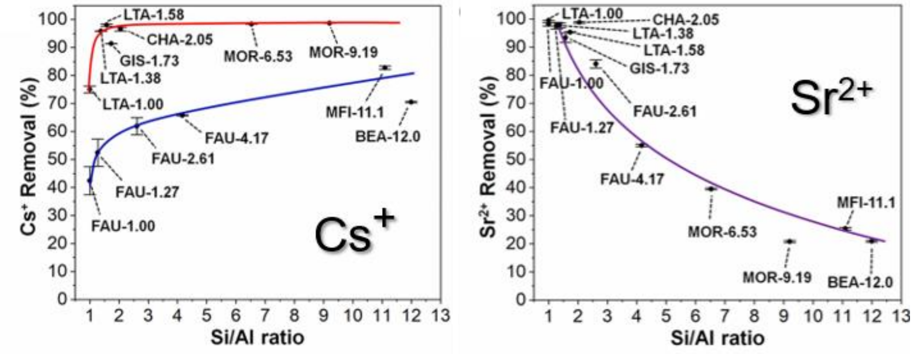
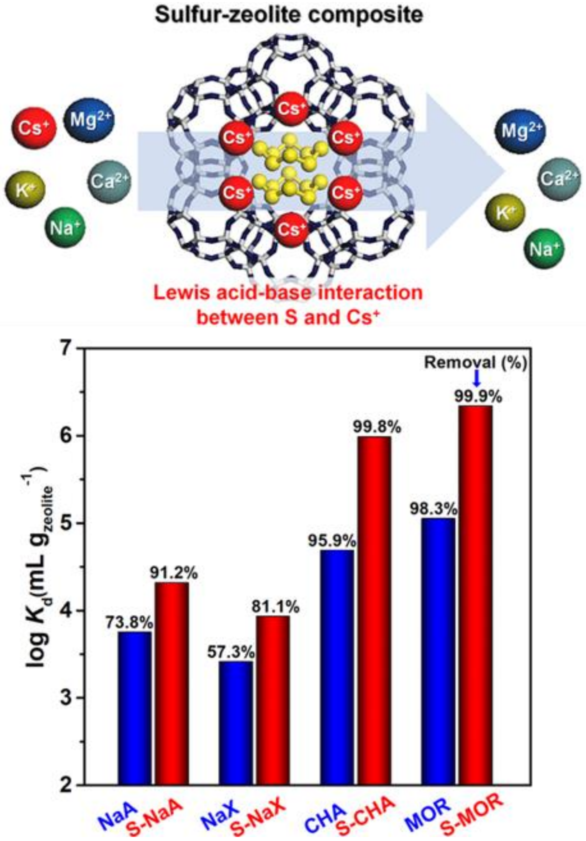


Image 2:



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New Synthetic Methods and Post-Synthetic Modification

FEZA21-OR-059

Two- and Three-Dimensional Finned Zeolite Catalysts

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Abstract Text: Confined channels and cages of zeolites have been widely used as shape-selective heterogeneous catalysts in the (petro)chemical industry. A common objective in the design of zeolite is to overcome the inherent mass transport limitations of micropores. The advent of two-dimensional[1] or self-pillared zeolites[2] exhibit superior catalytic performance to conventional analogues. In this presentation, we will describe an alternative approach to reduce the internal diffusion limitations of zeolites via the introduction of fin-like protrusions on zeolite surfaces by secondary growth. We will discuss the synthesis of multiple frameworks with nano-sized fins (size α) which exhibit an identical crystallographic registry with the interior crystal (size β) and show their superior catalytic performance relative to conventional materials.[3]

This new class of mass transport enhanced zeolites were synthesized by secondary growth using finely tuned compositions that allow for the epitaxial growth of fins on the surface of seed crystals. Here, we will discuss examples of several finned zeolites with disparate 2- and 3-dimensional pore networks to demonstrate the broader applicability of this approach. As proof of concept, we also apply this technique to commercial zeolite samples wherein we show that finned analogues improve catalyst performance. This work combines novel synthesis and catalyst testing (e.g. methanol to hydrocarbon and 1-butene isomerization reactions) with state-of-the-art characterization using techniques such as high-resolution electron tomography, operando spectroscopy, novel acid titration methods, and molecular modeling to correlate structural features of finned zeolite catalysts with their diffusion properties and enhanced activity, selectivity, and catalyst lifetime.

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New Synthetic Methods and Post-Synthetic Modification

FEZA21-OR-060

Computational screening of structure-directing agents for the synthesis of pure silica ITE zeolite

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Abstract Text: In this study we have focused on the prediction of potential molecules that can act as structure directing agents (SDAs), to synthesize the ITE zeolite with SiO2 composition. The approximation used is that appropriate SDAs will maximize shaping zeolite micropore, leading to a high van der Waals stabilization zeo-SDA intermolecular energy.

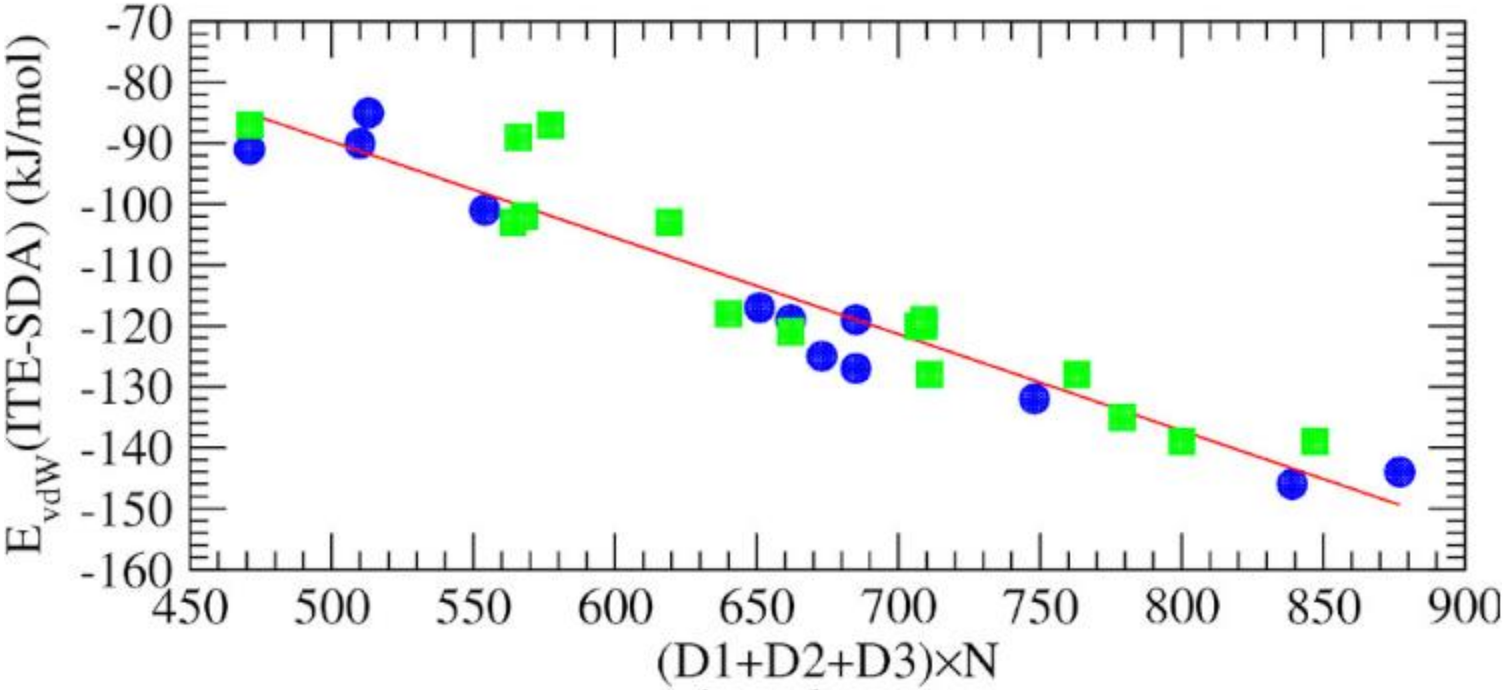
We used SciFinder[1] database, from which we obtained 2800 molecules that can be potential SDAs (SDA database) for the synthesis of zeolites. Second, we generated a new algorithm named shoebox[2], which performs the computation necessary to obtain the minimum volume box (shoebox) to enclose the molecule. This gives three perpendicular lengths (D1, D2, D3) that characterize the SDA size. Firstly, shoebox worked with a list of SDAs which synthesized ITE zeolite in pure silice according to literature. With this training set, a list of appropriate shoebox parameters (D1, D2, D3) was obtained. Third, using the latter parameters across the SDA database a new set of candidate SDAs was obtained.

In order to assess how good is the computer-generated set of SDAs (green squares), compared to the literature set of SDAs (blue circles), we plot both sets in the same graph (Image 1) with respect to a new parameter related to the SDA size, N×(D1+D2+D3), with 'N' being the number of atoms. The 'ability' to work as a good SDA is represented by the zeo-SDA stabilisation energy, which is also present in the plot. This energy is calculated by the new software zeoTsda [3], which automatically fills the zeolite micropore with as many SDA molecules as possible trying to find their minimum energy configuration using a combination of monte-carlo+lattice-energy-minimization.

Image 1 shows that, in the interval of maximum energy stabilisation (between 750-900 in the x-axis), there are as 4 computer-generated SDAs and 3 literature SDAs. This shows a good relative rate of success. Other regions of the plot, with less favourable energies, do contain a similar density of 'computer-generated' and 'literature' SDAs, indicating that the quality of both sets is very similar. This does not ensure the new suggested SDAs will necessariyl drive the syhthesis to ITE but at least they look like reasonable alternatives. More details, not included here, regarding the competition with RTH zeolite can be found in our recent study [2].

Image 2 shows an example of computer designed SDA that is suggested as candidate for the synthesis of pure silica ITE zeolite.

Image 1:



-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
450
500
550
600
650
700
750
800
850
900
E_{vdW}(ITE-SDA) (kJ/mol)
(D1+D2+D3)×N

Image 1

Image 2:

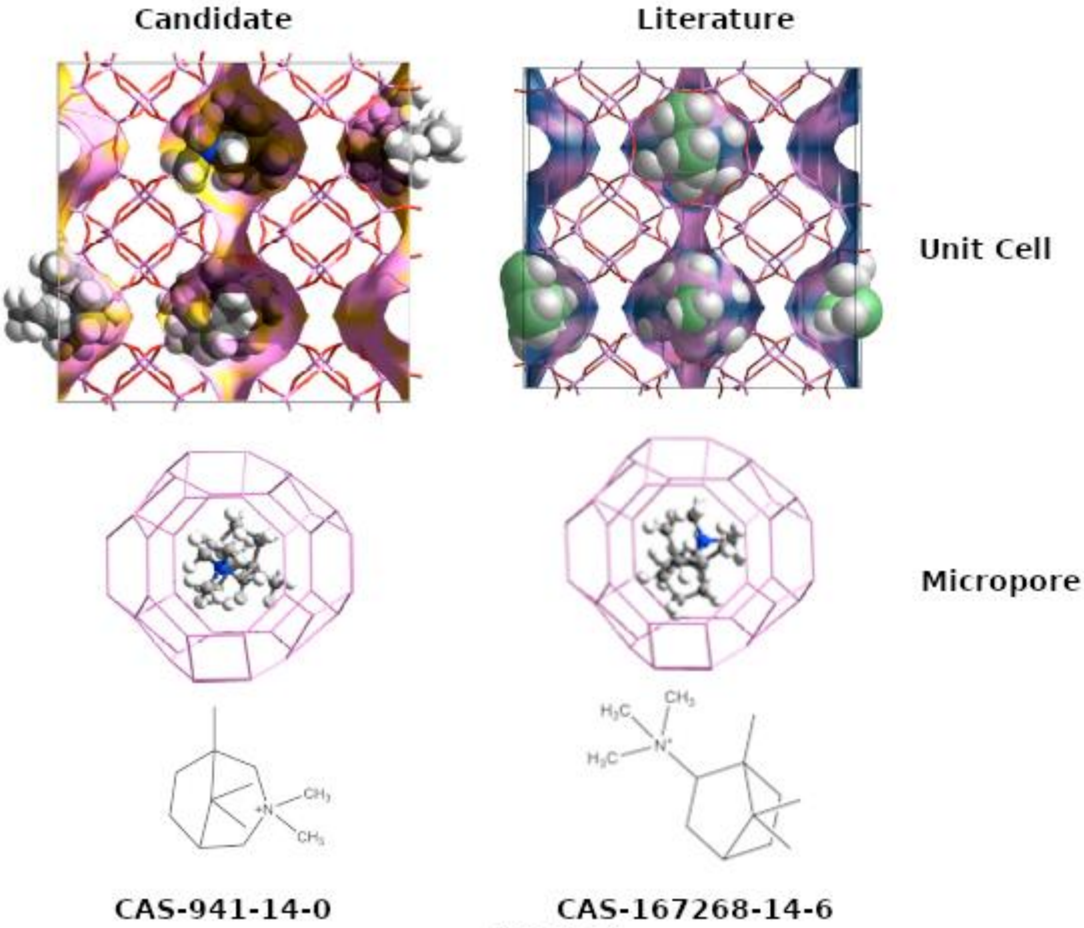


Image 2

References: [1] https://www.cas.org/.

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New Synthetic Methods and Post-Synthetic Modification|Zeolites/Inorganic materials

FEZA21-OR-062

Structural Stabilization and Diversity of Germanosilicates

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Abstract Text: 1. Introduction

Germanosilicates, an important zeolite family with attractive structures but limited hydrothermal stability, meet with great obstacles in practical application due to the easy hydrolysis of Ge-O bonds. A facial and versatile method is developed in the present study to substitute isomorphously Ge atoms for Si atoms, giving highly stable siliceous analogs to the pristine germanosilicates.[1] Germanosilicate UTL zeolite experienced unusual orientated collapse and reconstruction during the structural stabilization process.[2] On the other hand, structural collapse and healing also occurred in the acid treatment of calcined UTL germanosilicate, which gave several structural derivatives with continuously tunable pore sizes.[3] In a particular case of CIT-13 germanosilicate, the structural evolution to novel diversities is preferred to be realized in mild alkaline treatment rather than acid medium.[4,5]

2. Experimental

Germanosilicates IM-12 was stabilized in 1 M HNO_3 solution at 463 K for 24 h. For Sn-UTL, the suspension were cooled down rapidly after the acid treatment for 45 min, and then a certain amount of $SnCl_4 \cdot 5H_2O$ were added. The obtained mixture were heated again for another 22.75 h. The calcined UTL zeolite was treated by 1 M HNO_3 solution at 463 K for 15 min - 2 h to produce different daughter structures. Ti active sites were then introduced by liquid-phase titanation with H_2TiF_6 aqueous solution. For 14*10-R CIT-13 germanosilicate, the structural diversities were realized in the $NH_3 \cdot H_2O$ aqueous solution. Two novel zeolites of 10R ECNU-21 and 12*8-R ECNU-23 were obtained by treating CIT-13 with 0.5 wt% and 1.0 wt% $NH_3 \cdot H_2O$ aqueous solution, respectively.

3. Results and Discussion

The high-temperature acid treatment of as-made Ge-rich IM-12 (Si/Ge=4.7) resulted in highly siliceous structure (Si/Ge=233), which exhibited the same XRD patterns with the pristine samples but much higher hydrothermal stability. The Rietveled refinement, Ar sorption and TEM images of stabilized IM-12(S) zeolite all confirmed the structure topology and pore system were the same as the pristine UTL zeolite. The IR and ^{29}Si NMR spectra suggested that the Ge-rich double-4-ring (*d*4*r*) units were transformed to siliceous ones. Thus, the stabilization process was realized by replacing the Ge atoms mainly in *d*4*r* units with Si atoms, well preserving the pristine structures (Figure 1A). This strategy was also successfully extended to BEC, IWR and UWY germanosilicates. Taking a deep investigation into the acid treatment of UTL zeolite, an unusual local structural collapse and reconstruction process was observed. Benefiting from this, Sn atoms were introduced to produce an extra-large pore Sn-UTL zeolite, which exhibited higher activities in the Baeyer-Villiger oxidation reactions of 2-adamantanone compared to Sn-Beta zeolites.

However, the acid treatment of calcined UTL zeolite produced several novel daughter structures with different interlayer pore sizes rather than stabilized analog. Ti atoms were then introduced to these daughter structures, giving (extra-)large pore titanosilicates with highly active performance in the epoxidation reactions of bulky cyclohexene (Figure 1B).

In the contrast, calcined CIT-13 germanosilicates cannot produce novel daughter structures in acid medium, due to the presence of a larger amount of stable Si-O-Si bonds in *d*4*r* units. The mild alkaline solution was effective in modifying the CIT-13 structure and gave two novel zeolites of ECNU-21 and ECNU-23 (Figure 2). ECNU-21 was a highly active catalyst in the hydration reaction of ethylene epoxide.

4. Conclusions

The high-temperature acid treatment of germanosilicates highly stabilized the crystalline structures without changing the pristine structural topology, which brings hope for the real application of germanosilicates. On the other hand, the structural diversities of germanosilicates by acid or alkaline treatment provide a new strategy for exploring novel zeolites.

Image 1:

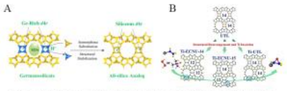

Figure 1. Structural stabilization (A) and modification (B) of IM-12 germanosilicate in acid medium.

Image 2:

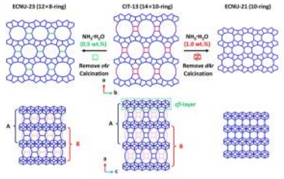

Figure 2. Structural modification of CIT-13 germanosilicate in mild alkaline solution.

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New Synthetic Methods and Post-Synthetic Modification|Zeolites/Inorganic materials

FEZA21-OR-063

2D-3D-3D transformation: ferrierite and omega zeolites from Na-RUB-18 layered silicate

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Abstract Text:

Synthetic zeolites have been widely preferred for industrial purposes because of their more uniform structure and composition, and the possibility to modulate some of their properties during the crystallization. In this way, new synthetic routes that start from other crystalline structures have been largely studied and considered interesting alternatives for the conventional procedures. Intuitively, hydrated layered silicates and even other zeolites were considered good precursors due to high structural similarity, even sharing one or more basic units.

This work proposes a hydrothermal synthesis route starting from the layered Na-RUB-18 to obtain zeolitic structures. Using the organic structure directing agents (OSDA) 1,3-diaminopropane or pyrrolidine, and different Si/Al molar ratios, ferrierite (FER) and omega (MAZ) zeolites were synthesized through a 2D-3D-3D transformation, sequentially. The conversion was based on the structural similarity between the precursor and the ferrierite zeolite, and then the evolution to a more stable phase, the omega.

Using Si/Al molar ratio equal to 7.5 and 1,3-diaminopropane as OSDA, a gradual transformation from Na-RUB-18 to FER zeolite was observed as the crystallization progressed (Figure 1, a). After 36 h, pure FER zeolite with Si/Al molar ratio equal to 9.6 was obtained, an indication that the aluminum added to the gel was not fully used during the transformation. The micrographs of this sample (Figure 2) showed FER crystals with unique layered habit, formed by thin aggregated layers with 10-50 nm. Finally, a phase mixture between FER and MAZ zeolites was obtained at any longer crystallization time.

The conversion to ferrierite using pyrrolidine was faster than when using 1,3-diamino propane as OSDA, and then led to a complete interzeolitic transformation to MAZ structure, (Figure 1, b). After 24 h pure FER was already obtained, without any trace of the lamellar precursor. At longer crystallization times, the MAZ characteristic peaks were gradually observed. Finally, after 168 h, pure MAZ was obtained. The FER and MAZ samples presented Si/Al molar ratios of 7.2 and 12.8, respectively, indicating that aluminum was eliminated from the solid upon the transformation.

Our synthesis procedure combined the structure directing capacity of 1,3-diaminopropane and pyrrolidine with the aluminum activating role over the lamella. Surface silanol groups are deprotonated at the reaction pH (> 12) and attack aluminum species, then forming the first reactive aluminosilicate units responsible for the conversion of the precursor into a zeolitic structure. The structural similarity between Na-RUB-18 and FER, which share the *mor* unit, allowed to propose a localized conversion, with the breaking and reorganization of two *mor* units that give rise to one *fer* unit. In its turn, the MAZ preparation cannot involve shared units since FER and MAZ have no structural similarity, therefore, the transformation would be associated with the progress of the reaction that leads to a more stable phase.

Acknowledgements:

The authors acknowledge to the Fundação de Amparo à Pesquisa no Estado de São Paulo – FAPESP (2013/25706-3 and 2014/06942-0) for the financial support. This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Finance Code 001.

Image 1:

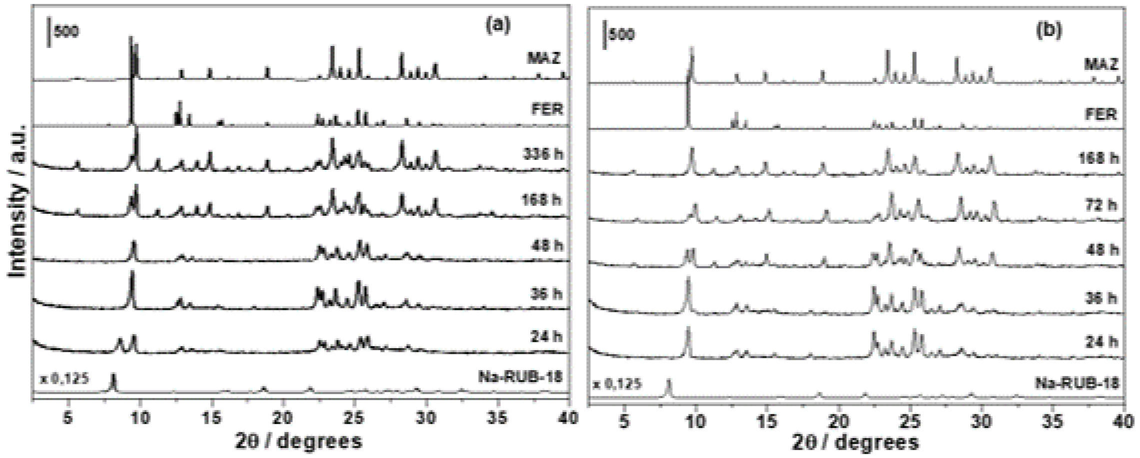

Figure 1. Powder x-ray diffractograms of the samples synthesized with Si/Al molar ratio equal to 7.5 and (a) 1,3-diaminopropane and (b) pyrrolidine as OSDA. Also, the Na-RUB-18, FER and MAZ simulated profiles.

Image 2:

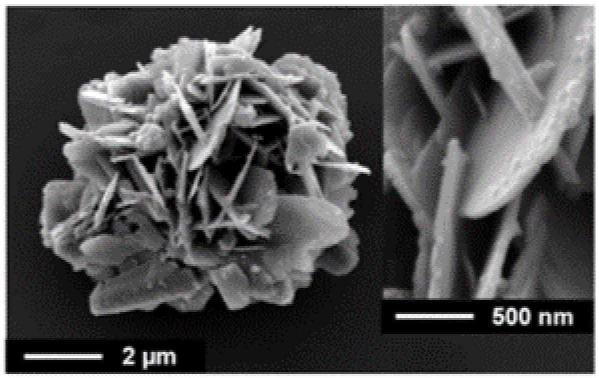

Figure 2. Scanning electron micrograph of the (b) FER sample obtained from 1,3-diaminopropane.

References:

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New Synthetic Methods and Post-Synthetic Modification|Zeolites/Inorganic materials

FEZA21-OR-064

Vapour-phase-transport technique for the synthesis of new zeolites by assembly-reassembly method

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Abstract Text: Zeolites are crystalline porous materials utilized for many applications including gas separation and catalysis. Up to now, the zeolite community recognizes about 250 different zeolite topologies despite the fact that millions of thermodynamically stable structures are predicted under ambient conditions. Such discrepancy between proposed zeolite topologies and those obtained via traditional hydrothermal approach initiated alternative strategies for zeolite synthesis. These novel strategies include both direct (e.g. using phosphorus-containing cations, metal complexes or proton sponges as structure-directing agents) and post-synthesis (3D-3D transformation at high pressures > 1 GPa; 3D-2D-3D transformation known as ADOR – assembly-disassembly-organization-reassembly) methodologies. However, most of the approaches use the same trial-and-error tactic, with the ADOR being the only exception [1]. The reason of ADOR uniqueness is that the topology of new zeolites can be easily predicted based on the knowledge of the parent structure. Although the ADOR strategy was successfully applied for the structural reconstruction of several germanosilicate zeolites such as UTL and UOV [1, 2], the respective transformation of other potential structures (in particular, IWW) was not successful up to date due to the high lability of respective zeolite layers containing pores perpendicular to the layer plane. It results either in complete degradation of the zeolite layers or, in the best case, in the reconstruction of initial zeolite framework with chemical composition different to that of parent material.

In this work, we succeeded with a straightforward strategy to construct new zeolites by employing a non-contact vapour-phase-transport (VPT) rearrangement at room temperature. This approach offers an opportunity to achieve novel zeolite topologies inaccessible by both hydrothermal and conventional ADOR synthesis routes. Diffraction, adsorption and microscopy data unambiguously proved that the transformation of IWW germanosilicate to the new zeolite phase (designated as IPC-18) proceeds without degradation of zeolite layers and thus affects exclusively interlayer structure units with no defects formed as the result of structural rearrangement. In situ XRD and XANES studies on the VPT rearrangement revealed the acid-induced reorganization of not only interlayer but also intralayer framework domains, resulting in the temporary disordering of the structure followed by its reconstruction to a well-ordered material with a different framework from the parent zeolite [3]. The successful application of VPT rearrangement to germanosilicate zeolites of different topologies highlights the potential of this technique for the 3D-3D transformation of crystalline materials with labile frameworks collapsing upon contact with the solvent (e.g., ordered organic-free germanates or some metal-organic frameworks).

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New Synthetic Methods and Post-Synthetic Modification|Zeolites/Inorganic materials

FEZA21-OR-065

Preparation of Hierarchical IWR Zeolites Based on Reassembly of Building Units

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Abstract Text: IWR-type framework zeolite with interconnected 12×10×10-membered-ring three-dimensional multi-pore system is of potential application in industrial catalysis processes, such as alkylation of aromatics.[1] Hierarchical zeolites have attracted much attention recent years, due to the faster access of bulky molecules to the active sites and consequently improved mass transfer within zeolite nanopores in contrast to the zeolites with single micropore structures.[2] In this contribution, we report a facile synthesis of hierarchical IWR zeolites based on reassembly of the building units produced from the decomposition of *BEA zeolite (used as heterogeneous seeds) and induced by choline molecules (used as organic structure-directing agent).[3]

In a typical synthesis, the molar ratio of the starting gel was 0.5 Choline: 1.1 SiO2: 0.5 GeO_2: 0.00125~0.02 Al_2O_3: 5 H_2O, where zeolite *BEA was used as aluminum source and/or heterogeneous seeds. The mixture was heated at 443 K for 7 days to accomplish the crystallization process.

As shown in **Figure 1**, IWR zeolites could be obtained from synthesis gels with initial molar ratios of Si/Al ranging from 25~400, although minor CDO zeolite as impurity could also be observed when Si/Al ratio was above 100. SEM images in **Figure 2** indicated IWR zeolites present unique house-of-cards-like stacking, consisting of nanosheet crystals with a typical thickness of 20~100 nm, length of 250~500 nm and width of 100~200 nm. The size of the crystals decreased with the increasing of Al content in the synthesis gel. The stacking of nano-crystals would generate hierarchical porosity, as shown in **Table 1**. The samples possessed high specific surface area. The extra specific surface area and mesopore volume of these samples rose as the decreasing of the Si/Al ratio in the products.

The XRD patterns (**Figure 3**) of the solid products obtained after heating the synthesis gel for different periods of time clearly demonstrated that the decomposition of *BEA zeolites occurred prior to the assembly of silicate and germanate species while CDO zeolite was an intermediate phase during the crystallization process. As proposed in **Scheme 1**, the crystallization of the IWR zeolite was believed to proceed through a novel cooperative structure-directing between choline and *BEA zeolite. The growth of IWR zeolite was ascribed to the reassembly of the building units produced from the decomposition of *BEA zeolite (including four-, five-, and six-membered rings units) and those induced by choline molecules (5-membered rings, 5MR units).

This work was supported by the National Key R&D Program of China (2017YFB0702800) and National Natural Science Foundation of China (21802168, 21972168).

Image 1:

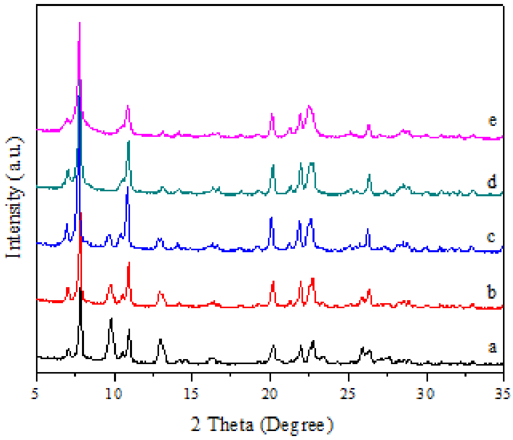


Figure 1. XRD patterns of IWR zeolite samples with variable initial Si/Al molar ratios: 400 (a), 200 (b), 100 (c), 50 (d) and 25 (e).

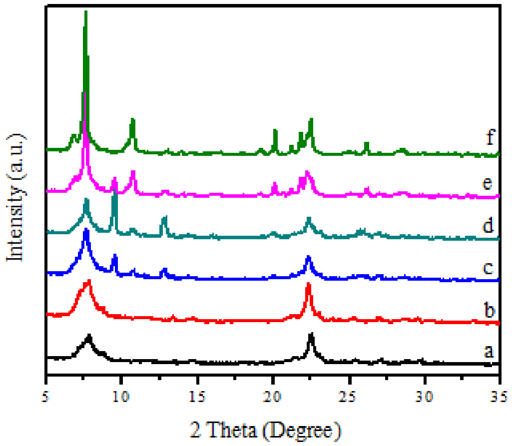


Figure 3. XRD patterns of solid products obtained after heating the synthesis gel for different periods of time: 0 h (a), 4 h (b), 12 h (c), 24 h (d), 72 h (e) and 168 h (f).

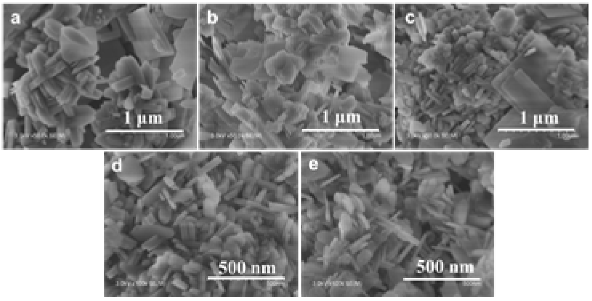
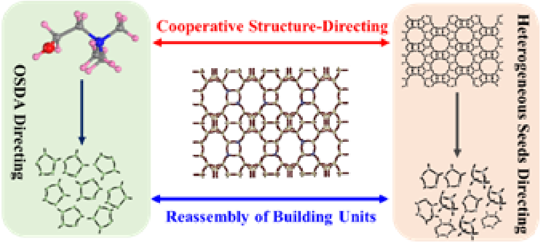


Figure 2. SEM images of IWR zeolite samples with variable initial Si/Al molar ratios: 400 (a), 200 (b), 100 (c), 50 (d) and 25 (e).



Scheme 1. The mechanism for preparation of IWR zeolite based on reassembly of building units.

Image 2:

Table 1 Textural properties of IWR zeolite samples.

Si/Al	S_{BET}[a] ($m^2 \cdot g^{-1}$)	S_{extra}[a] ($m^2 \cdot g^{-1}$)	V_{total}[b] ($cm^3 \cdot g^{-1}$)	$V_{micro.}$[a] ($cm^3 \cdot g^{-1}$)	$V_{meso.}$[c] ($cm^3 \cdot g^{-1}$)
400	403	37	0.37	0.15	0.22
200	501	39	0.44	0.18	0.26
100	527	45	0.47	0.19	0.28
50	568	54	0.49	0.20	0.29
25	552	77	0.52	0.19	0.33

[a] Analyzed by BET and *t*-plot methods. [b] Determined at $p/p_0 = 0.99$. [c] $V_{meso.} = V_{total.} - V_{micro.}$

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New Synthetic Methods and Post-Synthetic Modification|Zeolites/Inorganic materials

FEZA21-OR-066

Generation of Subnanometric Metal Clusters in Zeolites and Their Evolution Behavior Under Reaction Conditions

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Abstract Text: 1. Introduction

Single metal atoms and metal clusters have attracted much attention thanks to their possibility as heterogeneous catalysts.[1,2] However, the generation of stable single atoms and clusters on a solid support is still challenging.[3] Recently, we report a new strategy for the generation of single Pt atoms and Pt clusters with exceptionally high thermal stability, formed within purely siliceous MCM-22 during the growth of a two-dimensional precursor of the zeolite into three-dimensional structure.[4] These subnanometric Pt species are stabilized in the zeolite, even after treatment in air up to 540 ^{o}C. Furthermore, we have studied the dynamic structural transformation of those subnanometric Pt species during reduction-oxidation treatments and under reaction conditions by environmental transmission electron microscopy.[5]

2. Materials and Methods

The Pt@MCM-22 was prepared by the transformation of 2D into 3D zeolite, using purely siliceous ITQ-1 as precursor. *In situ* electron microscopy experiments were performed using a Titan 80-300 Environmental Transmission Electron Microscope at the Centre for Functional Nanomaterials (CFN), Brookhaven National Laboratory. The preparation for Pt@MCM-22 can also be extended for Au@MCM-22 and Pd@MCM-22, in which subnanometric Au and Pd clusters can be encapsulated in MCM-22 zeolite.

3. Results and Discussion

Subnanometric Pt species are finely dispersed in MCM-22 crystallites. With the help of aberration-corrected electron microscopy, we are able to directly measure the size of those Pt species and figure out their position in the zeolite. Some of the Pt atoms and clusters are located in the surface "cups" of MCM-22 and some of them are anchored to the zeolite framework. (see Figure 1) Nevertheless, a large part of subnanometric Pt species are located in the internal space of the structure, which is confirmed by the size-selective hydrogenation of propene and isobutene. These encapsulated subnanometric Pt species show higher activity than Pt nanoparticles for propane dehydrogenation reaction and more importantly, higher stability during the reaction-regeneration cycles.

Furthermore, using Pt@MCM-22 material as a model system, we have studied the evolution of Pt single atoms and clusters during reduction-oxidation treatments and under reaction conditions by ETEM. Pt nanoparticles and clusters will disintegrate into smaller clusters or even single atoms after calcination in O_2. And single atoms and clusters will agglomerate into small particles after reduction by H_2. Besides, it can be a general phenomenon that subnanometric metal species will undergo dynamic structural evolution under reaction conditions ($CO+O_2$, $CO+H_2O$, CO+NO and $NO+H_2$). For the same reaction, the states of metal species are dependent on the temperature and atmosphere.

The subnanometric Au clusters stabilized in MCM-22 zeolite also show excellent activity for aerobic oxidation of cyclohexane to KA-oil[6].

Figure 1. High-resolution STEM image of Pt@MCM-22 sample, showing the presence of single Pt atoms and subnanometric Pt clusters in the MCM-22 zeolite crystallites.

Figure 2. Comparison of the dynamic evolution of subnanometric Pt species under different reaction atmosphere from low temperature to high temperature.

4. Significance

Subnanometric Pt species (single atoms and clusters with a few atoms) with exceptional high stability can be generated and stabilized in MCM-22 zeolite. Those subnanometric Pt species show dynamic structural transformation during reduction-oxidation treatments and under reaction conditions. This method can be extended to other metals such as Au and Pd, which also show distinct catalytic properties compared to their nanoparticulate counterparts.

Image 1:

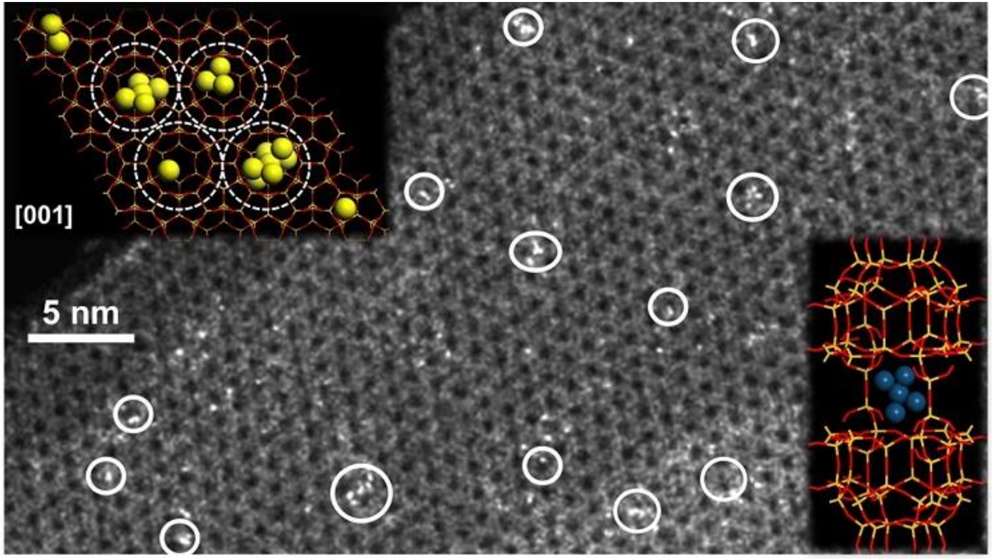
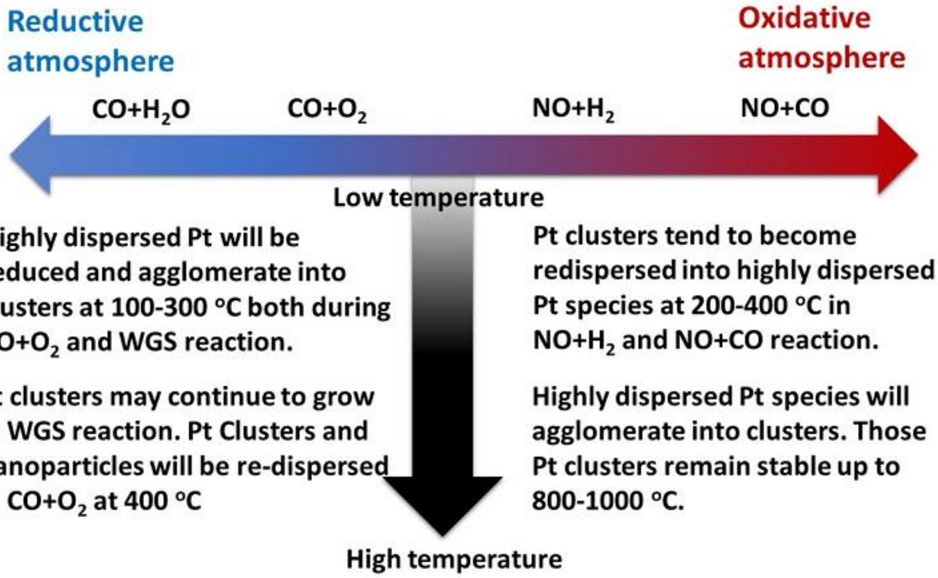


Image 2:



Highly dispersed Pt will be reduced and agglomerate into clusters at 100-300 °C both during CO+O$_2$ and WGS reaction.

Pt clusters may continue to grow in WGS reaction. Pt Clusters and nanoparticles will be re-dispersed in CO+O$_2$ at 400 °C

Pt clusters tend to become redispersed into highly dispersed Pt species at 200-400 °C in NO+H$_2$ and NO+CO reaction.

Highly dispersed Pt species will agglomerate into clusters. Those Pt clusters remain stable up to 800-1000 °C.

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New Synthetic Methods and Post-Synthetic Modification|Zeolites/Inorganic materials
FEZA21-OR-067

Development of Ultrafast Methods for Post-synthesis Modifications of Zeolites

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Abstract Text:

Development of Ultrafast Methods for Post-synthesis Modifications of Zeolites

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Zeolites are typically synthesized *via* the hydrothermal treatment, which typically takes several days and is operated in batch. In recent years, the continuous flow process, which is close to *plug-flow reactor* (rather than *continuous stirred-tank reactor*) in the concept of chemical reaction engineering, has experienced a fast development as it offers many merits over the batch. Switching the synthesis of zeolites from the batch operation to the continuous flow one, however, is a daunting challenge primarily because of the long synthesis time. Recently, our group has established an ultrafast route for zeolite synthesis.[1,2] The synthesis periods for a series of important zeolites were shortened to tens of or several minutes, which are in stark contrast to several days that are required (**Fig. 1**). The continuous flow synthesis of zeolites was further established based on the ultrafast synthesis.

Post-synthesis modifications are important and sometimes indispensable approaches to render zeolites with compositional, structural and morphological features that are not easily obtained through its direct synthesis. Some post-synthesis modifications of zeolites are carried out in a solution-mediated environment, which resemble the hydrothermal synthesis and consume an equivalent or even longer time. Establishing ultrafast routes for post-synthesis modifications of zeolites is thus of significance to efficiently generating zeolites with specific properties and remarkably enhancing their performance in applications. On the basis of the ultrafast synthesis, we recently discovered that some post-synthesis modifications of zeolites could proceed extremely fast under certain conditions. This finding allowed for the establishment of ultrafast methods of post-synthesis modifications to prepare nanosized zeolite,[3] core-shell structured zeolite[4] and hierarchical zeolite with uniform mesopores[5] (**Fig. 2**). Only a few minutes were needed to create the target features through the ultrafast post-synthesis modifications, which were considerably shorter than that are required in the conventional methods. In this contribution, we present our efforts on developing such ultrafast post-synthesis approaches and discuss the potential consequences of this methodology to the preparation of catalysts with tailor-made properties.

Figure captions:

Fig. 1 Ultrafast synthesis of zeolites in the tubular reactor.

Fig. 2 Ultrafast methods of post-synthesis modifications to prepare zeolites with specific features. Examples: (a) SEM image of a nanosized SSZ-13 prepared by combining post-synthesis milling with an ultrafast recrystallization in the tubular reactor for 10 min;[3] (b) SEM image of a core-shell structured zeolite prepared by an ultrafast epitaxial growth of silicalite-1 layer over a ZSM-5 core in 5 min;[4] (c) TEM image of a USY zeolite with uniform mesopores prepared by ultrafast reconstruction of mesopores in a CTAB-containing alkaline solution.[5]

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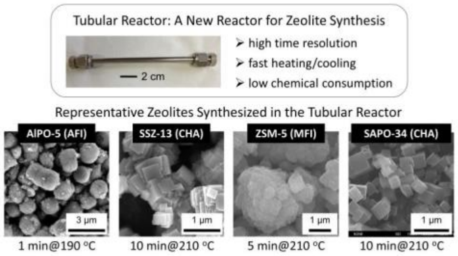
Image 1:



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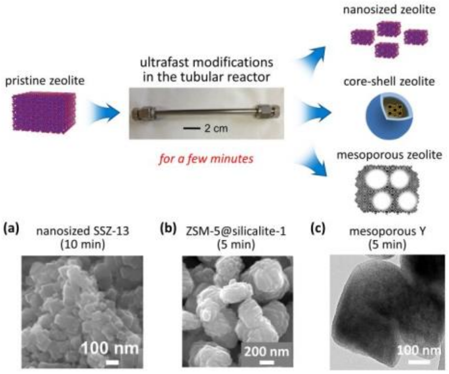

New Synthetic Methods and Post-Synthetic Modification|Zeolites/Inorganic materials

FEZA21-OR-068

Synthesis and catalytic performance of the P-modified Al- and Ga-containing ITQ-52 zeolite

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Abstract Text: Introduction

The zeolite ITQ-52 (IFW) presents a tridirectional pore system of 8- and 10-ring channels that intersect one to each other forming large cavities. The zeolite IFW has been obtained only as borosilicate by using as Organic Structure Directing Agent (OSDA) an aminophosphonium cation (zeolite ITQ-52) [1] or a dicationic tetraalkylammonium (zeolite SSZ-87). [2] Here, we report the first direct synthesis of aluminium- and gallium-containing ITQ-52 using an aminophosphonium cation as OSDA, the post-synthesis treatments for controlling the extra-framework phosphorus species and the catalytic performance in the MTO reaction.

Experimental

Zeolites ITQ-52 were obtained from synthesis gels having the following composition: (1-(x+y)) SiO_2 : x B_2O_3 : y Y_2O_3 : 0.2 OSDA : 7.5 H_2O : 0.04 Seeds, where x and y were varied from 0-0.0325 keeping constant x+y=0.0325, Y_2O_3 is Al_2O_3 or Ga_2O_3, OSDA is 1,4-butanediyldi[tris(dimethylamino)] phosphonium hydroxide and some B-ITQ-52 crystals were used as seeds. The synthesis gels were heated at 150˚C for 5 days under continuous rotation (40 r.p.m.). The as-made samples were heated at 600˚C for 5 h in a stream of 20v/v% of H_2 in N_2 and subsequently, in air, some samples were washed with an aqueous ammonium acetate solution at different temperatures for 2 hours and calcined in air at 550˚C. The MTO reaction was carried out at 400˚C and the weight hour space velocity (WHSH) was $0.5h^{-1}$.

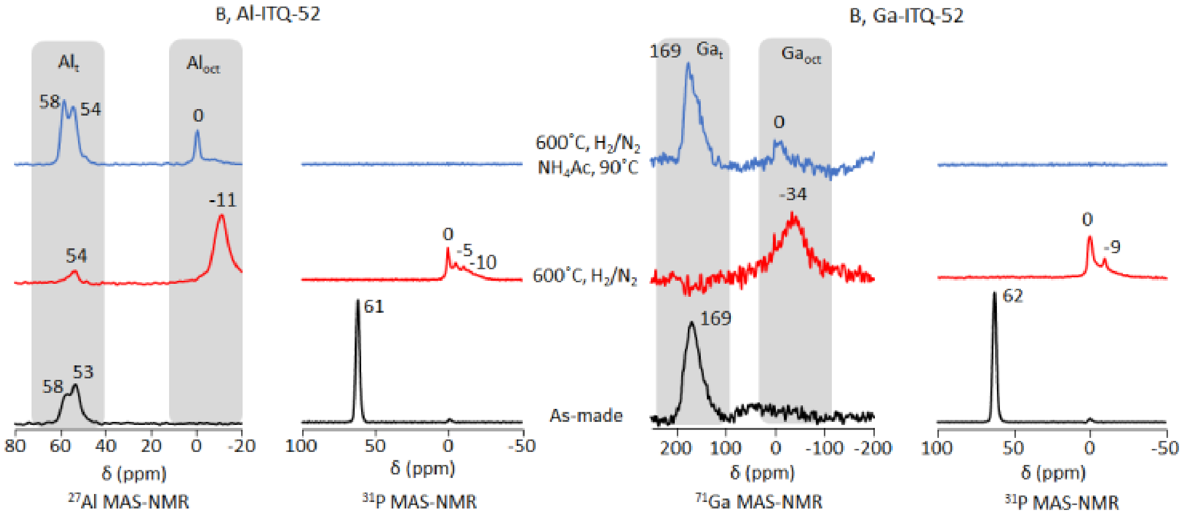
Results and discussion

The zeolite ITQ-52 has been prepared by direct synthesis as boroaluminosilicate (Si/Al = 18.6 – 206) and borogallosilicate (Si/Ga = 95 – 335). The incorporation of Al and Ga atoms in framework positions and the presence of OSDA molecules in the solid were confirmed by employing ^{27}Al, ^{71}Ga and ^{31}P MAS-NMR spectroscopy (Fig. 1). The heat treatment of the as-made samples resulted in the decomposition of the OSDA molecules and the formation of extra-framework P_xO_y species. The ^{31}P MAS-NMR spectra of the thermal treated Al- and Ga-ITQ-52 zeolites show resonances centred at 0 and -5 ppm assigned to the presence of phosphoric and pyrophosphoric acids, while, the broad signal centred around -10 ppm is associated to P_xO_y species that are interacting with octahedral coordinated Al or Ga located in framework positions, that appear at -11 and -34 ppm in the ^{27}Al and ^{71}Ga MAS-NMR spectra, respectively. The full removal of P-species by washing treatments allowed recovering the tetrahedral coordination of Al and Ga, showing in the ^{27}Al and ^{71}Ga MAS-NMR spectra a similar profile to that obtained for the as-made samples (Fig. 1), suggesting reversible octahedral coordination of Al and Ga in the presence of extra-framework P-species.

The Al- and Ga-containing ITQ-52 having different P content were tested in the MTO reaction. The catalytic results showed a clear influence of the presence of extra-framework P species in the selectivity and activity of the catalysts. Showing a maximum selectivity to light olefins (ethylene and propylene) of 60% when P/Al=0.17 (Si/Al=125) and P/Ga=0.14 (Si/Ga=148).

Fig. 1. ^{27}Al, ^{71}Ga and ^{31}P MAS-NMR spectra of the as-made B,Al-ITQ-52 (Si/Al=91) and B,Ga-ITQ-52 (Si/Ga=81), after heat treatments and after washing at 90˚C. The grey shadows show the characteristic region of the Al and Ga in tetrahedral (Al_t and Ga_t) and octahedral (Ga_{oct} and Ga_{oct}) coordination.

Image 1:



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New Synthetic Methods and Post-Synthetic Modification|Zeolites/Inorganic materials

FEZA21-OR-069

Synthesis of embryonic zeolites with controlled physicochemical properties

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Abstract Text: Molecular sieve zeolites are widely used as heterogenous catalysts in many industrial processes. They typically offer high surface area, uniform micropores with well-defined topology, strong acid sites, and high thermal and chemical stability. The unique property of zeolite materials is the shape selectivity, which is a consequence of the confinement of the active sites in well-defined micropore space. However, the sole presence of micropores often imposes transport limitations of reactants and products, in particular, those with a size close to the pore diameter. This issue is particularly crucial for refining industries where the demand to treat heavy oil fractions became urgent. Hence, zeolites with extra-large pores are highly desired.

In our previous work, we proved that the semi-formed zeolite units, denoted embryonic zeolites (EZ), present a superior catalytic performance in the conversion of a bulky molecule model with respect to their crystalline counterparts.[1] They offer larger and highly accessible micropores with respect to conventional zeolites. In addition, they survive high temperature treatment and exhibite moderate acid strength. Here, we report the control of their physicochemical properties by using organic structure directing agents of different size: tetramethylammonium hydroxide (TMA), tetrabutylammonium hydroxide (TBA), trimethyladamantylammonium hydroxide (TMAd) and tetrahexylammonium hydroxide (THA). All prepared samples are X-ray amorphous, **Figure 1A**. According to the experimental data, the larger the template, the higher the microporous volume of the specific surface area and the lower the acidity of the embryonic zeolites, **Figure 1B**. Their catalytic performances were evaluated in the dealkylation of 1,3,5-Triisopropylbenzene. The results given in **Figure 1B** show that an appropriate combination between accessibility and acidity leads to high catalytic activity.

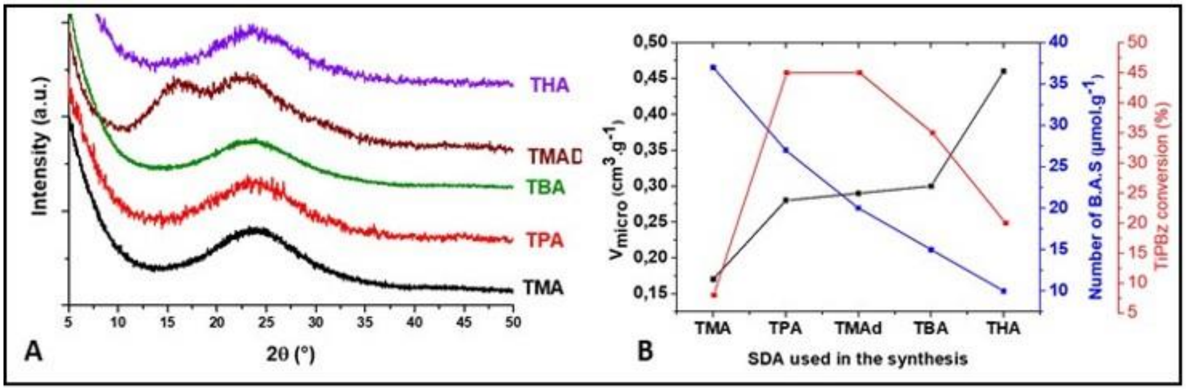
The EZ physicochemical properties were also controlled by changing the synthesis conditions (time, temperature, synthesis duration) and by introducing some heteroatoms (Mo, Fe, Cu,…). The extension of the crystallization time leads to an increase in the particle size, and it is combined with textural changes. More precisely, an increase in surface area and microporous volume is observed. However, this trend changes with the appearance of first crystals; with the advancement of the crystallization, a decrease in the V_{micro} and S_{BET} is observed. Also, a different acidity and subsequently, a different catalytic activity of these precursors was observed. The results of this study will be used for the preparation of zeolitic embryos with variable surface and textural properties, micropore volume, acid strength and oxidation properties. Detailled information on all aspects related to the synthesis and the control of the physicochemical properties of the EZ will be provided.

Acknowledgments:

The financial support from TOTAL Research and Technology Feluy, Belgium (TRTF) and the Industrial Chair ANR-TOTAL “Nanoclean Energy” is highly appreciated. V.V. and S.M. acknoweldege the finanicail support from the CARNOT project ESP 3DNANOZET 5281.

Figure 1: (A) XRD patterns of EZ and (B) 1,3,5-TiPBz conversion, number of Brønsted acid sites and micropore volume of EZ as a function of OSDA used in the synthesis. Catalytic test conditions: T = 300°C, WHSV = 8h^{-1}, TOS = 2 min.

Image 2:



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New Synthetic Methods and Post-Synthetic Modification|Zeolites/Inorganic materials

FEZA21-OR-071

Selective demetalization of amphiphilic zeolites in oil/water emulsion

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Abstract Text: Hierarchical meso-micro-porous zeolites can facilitate the diffusion of bulky molecules and increase the accessibility of active sites. Top-down approaches (*e.g.* post-synthetic modifications) are widely used to introduce hierarchical mesopores to zeolites. Although being simple and effective, the controllability of post-treatment is unsatisfactory, as the mesopores are often in the form of disordered or random cavities (which may lead to less effective molecular diffusion). To achieve minimum diffusion/transport resistance, the hierarchical zeolites should be optimized with the ordered and well-ranked hierarchical porous structure. However, the fabrication of zeolites with the ordered hierarchical of pore system via the post-synthetic routes remains challenge, since the formation of mesopores is often unselective. To achieve the controllable creation of mesopores using the post-synthetic method, a biphase system may be beneficial to tailor the distribution of alumina in zeolite crystal during the hydrothermal treatments. Herein, Al-rich faujasite (FAU) Y zeolite is “partially” functionalized by hydrophobic silane to form amphiphilic particles with hydrophilic head (hydroxy groups on zeolite surface) and hydrophobic tail (long alkyl chain). Mesopores are introduced by sequential post-synthetic dealumination and desilication in biphase oil/water systems. Since dealumination only occurs in water phase, the alumina is selectively extracted from the hydrophilic part of zeolite, which leads to the formation of alumina gradient. The alumina gradient could further induce the formation of hierarchical mesopores during the desilication process. In this presentation, we will report the details of the method developed together with the comprehensive and comparative characterization of the resulting materials, regarding the textural property, morphology, diffusional and catalytic performance.

New Synthetic Methods and Post-Synthetic Modification|Zeolites/Inorganic materials

FEZA21-OR-072

Influence of postsynthesis treatments on acid site strength of ZSM-5

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Abstract Text: Introduction

Many organic reactions (Friedl-Crafts type, ring transformation, halogenation, condensation, isomerization, etc.) can be catalysed by solid acid catalyst. Among them, zeolites have been often used, due to the known nature of the active (acid) sites. It makes them unique catalysts in comparison with others such as metals, metal oxides, and sulphides. Conventional solid acids, (zeolites such as ZSM-5, USY, beta) of micrometer sized crystal, are model system for research of the relationship among their selectivity, activity, and deactivation in the polyolefins cracking, MTO conversion, methane dehydroaromatization, etc. At the same time, it shows importance of the accessibility of active sites to the larger molecules, due to steric and diffusion limitations.

Experimental

The ZSM-5 (MFI) was prepared using simple, classical hydrothermal synthesis. starting from the synthesis gel with molar composition:

0.10 Na_2O – 0.08 TPABr – 1.00 SiO_2 – 0.02 Al_2O_3 – 20.00 H_2O.

First, NaOH was dissolved in of distilled water, then $Al(OH)_3$ and TPABr were added to the basic solution. Than precipitated SiO_2 was added. Resulting gel was stirred for 1 hour at room temperature and kept in oven at 175 °C for 5 days in teflon-lined stainless steel autoclaves, under static conditions. After synthesis, product was washed, dried at 105°C and calcined in air at 550°C - to eliminate SDA. The H-form was obtained after two cycles of ion exchange with 1 M NH_4Cl (1 h each) followed by a calcination at 550°C. Desilication of the HZSM-5 was made using 0.2 M NaOH solution for 45 min at 65 °C, with stirring, and again transformed to H-form as described above.

Results and discussion

PXRD patterns show that all postsynthesis treatments (first desilication with NaOH solution, then wet impregnation (with Ag^+, Mg^{2+}, and Fe^{3+}), than reassembly in reactor, and finally calcination) have not significant influence on crystallinity of the samples. At the same time, mesoporosity after dealumination increases about 4 times (Fig. 1). In comparison to starting material (HZSM-5) total amount of acid places decrease after desilication from 565.56 µmol/g to 523.83 µmol/g, to 509.77 µmol/g in Mg-ZSM-5, 485.21 µmol/g in Fe-ZSM-5, and surprisnigly increase to 590.64 µmol/g in Ag-ZSM-5. The ratio between the number of strong (NH_3 desorption around 400 °C) and weak acid sites (NH_3 desorption around 230 °C) significantly decrease in following order: HZSM-5 > desilicated HZSM-5 > Mg-ZSM-5 >. Fe-ZSM-5 > Ag-ZSM-5 (Fig 2), what is also confirmed by vacuum FTIR spectroscopy.

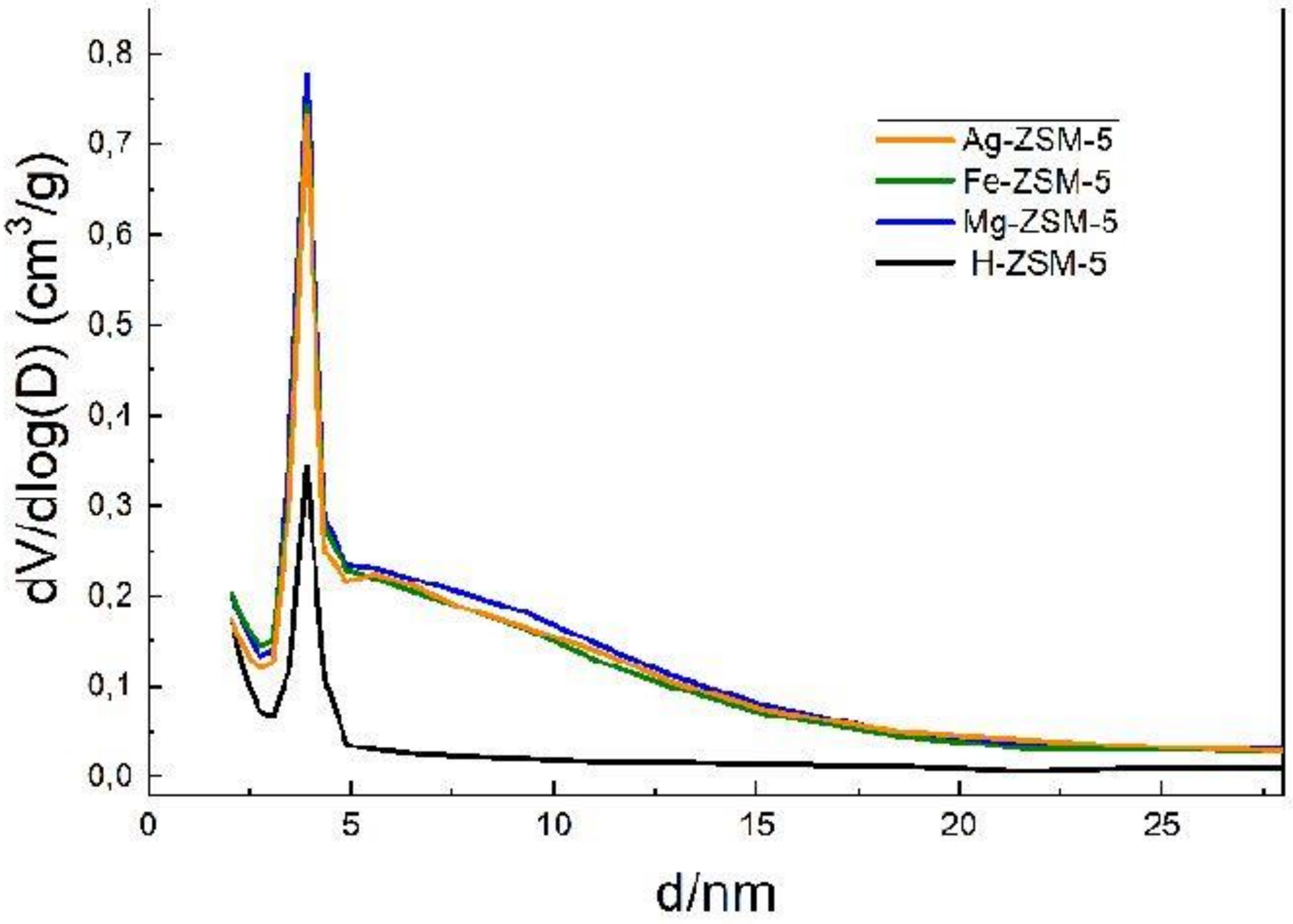
The distribution of pores measured by nitrogen adsorption/desorption (BJH) of ZSM-5 crystals before (H-ZSM-5) and after postsynthesis treatment – desilication (parent), wet impregnation (Ag, Fe, Mg) and consecutive thermal treatment of samples were shown in Fig. 1., while NH_3-TPD profiles of ZSM-5 samples before and after postsynthesis were shown in Fig. 2.

Conclusions

Introduction of the various metal cations into hierarchical ZSM-5 does not have influence on samples crystallinity, but significantly affects the ratio between weak and strong acid sites, mainly decreasing the number of strong acid sites, what was measured by NH_4-TPD, and confirmed by vacuum FTIR spectroscopy.

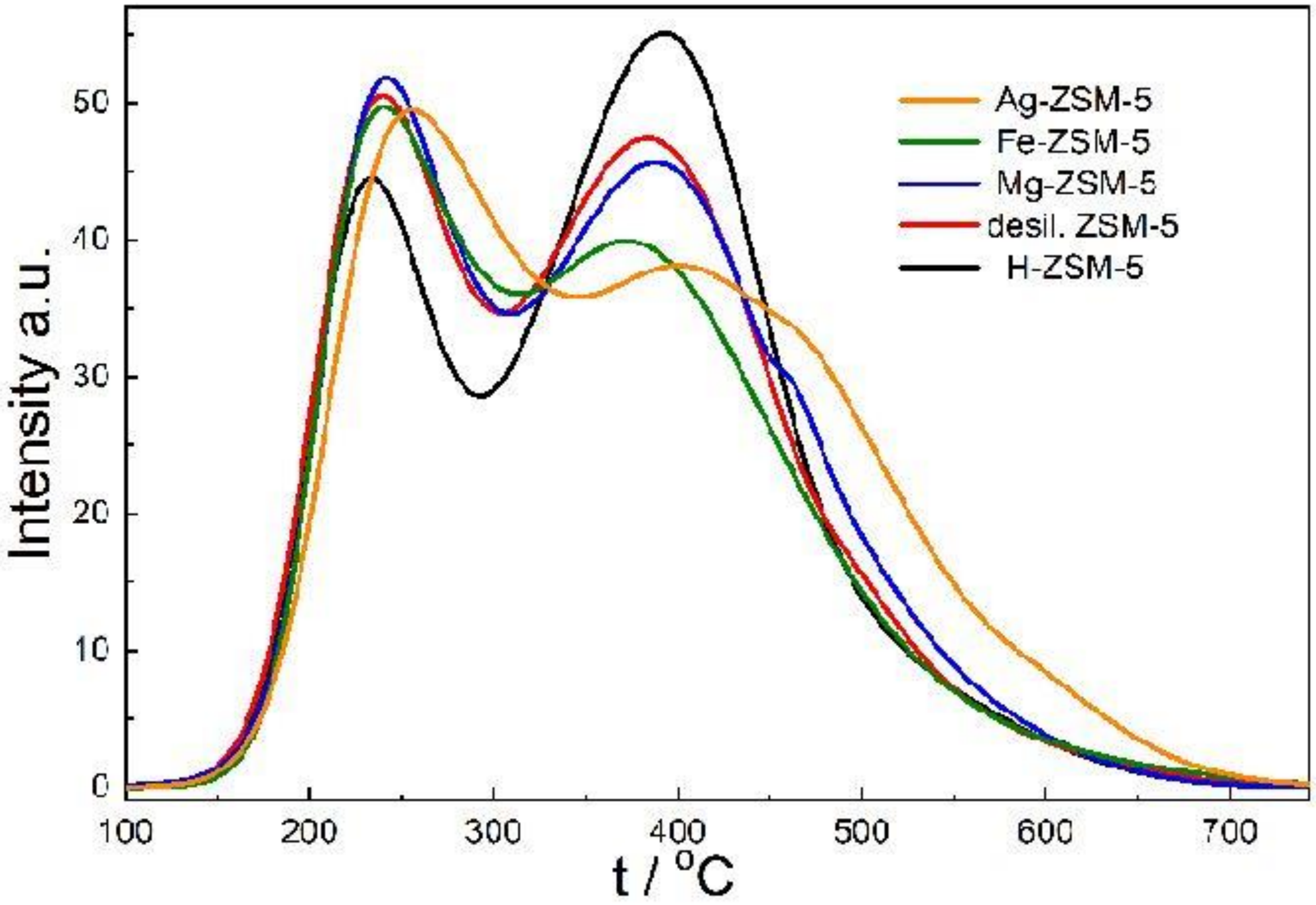
Acknowledgement: This work was supported by Croatian National Science Fundation, Project no. IP2016-06-2214

Image 1:



0,8
0,7
0,6
0,5
0,1
0,3
0,2
0,1
0,0
0
5
10
15
20
25
dV/dlog(D) (cm^3/g)
d/nm
Ag-ZSM-5
Fe-ZSM-5
Mg-ZSM-5
H-ZSM-5

Image 2:



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New Synthetic Methods and Post-Synthetic Modification|Zeolites/Inorganic materials

FEZA21-OR-073

One-pot synthesis of iron containing SSZ-13 zeolites with record methanol productivity in methane oxidation

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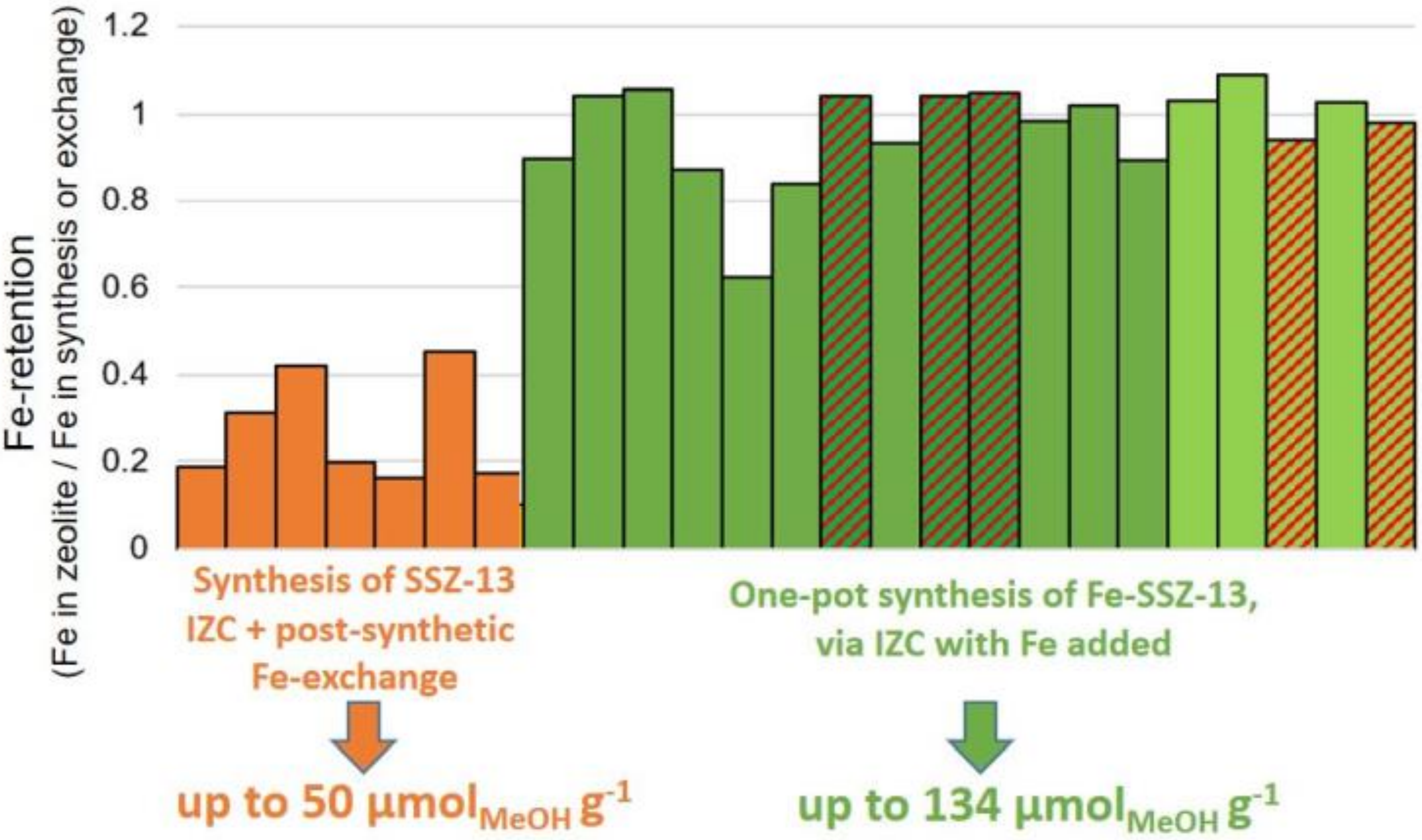
Abstract Text: C-H activation on transition metal containing zeolites, exemplified by the partial oxidation of methane, is an important catalytic challenge in need of efforts on multiple fronts.[1,2] Recently, in the iron-containing line of materials, i.e. those requiring N_2O as oxidant, the α-Fe active site in SSZ-13 (CHA) was found and elucidated, with no spectator species observed, besides few inactive Fe-oxides.[3] The classic way of incorporating Fe in such small-pore cage-containing zeolites[1] happens post-synthetically via ion-exchange and related procedures. Although recently, the synthesis of CHA host zeolites enriched with Al-distributions capable of hosting α-Fe were unravelled by our group[4], there seems to be a large limit to the iron loadings one can achieve post-synthetically. Using post-synthetic methods, Fe retentions higher than 45% could not be achieved (and usually even <30%), even when consecutively repeated and from different Fe-precursors (Image 1, green, left). The present work demonstrates the utility of 'one-pot' preparations (similar to a strategy used in SCR)[5] of iron-containing small pore CHA zeolites, allowing complete Fe-retention and methane partial oxidation productivities that are multiple times higher than those for the conventional post-synthesis Fe-loaded zeolites.

Specifically, under carefully screened conditions, pure SSZ-13 crystallization is still possible with relatively large Fe contents (Fe/Al: 0.2 – 0.45, Si/Al: 15) in the synthesis mixtures. These 'one-pot' strategies can proceed in very high yields (>0.9) and with nearly 100% Fe retention (Image 1, orange, right). While FAU-to-CHA interzeolite conversion (IZC) methods can be used, the high retention and activity can also be achieved independent of the T-atom sources (e.g. amorphous silica and Al-hydroxides also work).

The 'one-pot' and 'post-synthetic benchmark' materials were subjected to rigourous characterization (DR-UV-VIS, Mössbauer spectroscopy, P-XRD, N_2-physisorption, elemental analysis, TGA) and the methane partial oxidation cycle. The methanol productivities, by extraction, for 'one-pot' samples can mount to 134 $\mu mol_{methanol}.g_{zeolite}^{-1}$, while for the most optimal post-synthetic material, less than 50 $\mu mol_{methanol}.g_{zeolite}^{-1}$ is encountered (and on average, less than 25). Besides these record-high values for Fe-systems, clues into how the a-Fe site forms in these materials were gathered. This led to a mechanistic hypothesis which includes the incorporation of Fe into the framework at first, followed by post-synthetic Fe mobility during calcination/activation.

In short, we will present a more clean and economic Fe-SSZ-13 preparation protocol and its mechanistic consequences, leading to much higher active site densities for methane partial oxidation.[6]

Image 1:



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[6] Manuscript in preparation.

New Synthetic Methods and Post-Synthetic Modification|Zeolites/Inorganic materials

FEZA21-OR-074

A combination of ADOR strategy and isomorphous substitution for the synthesis of model zeolite catalysts to examine pore size−activity relationship

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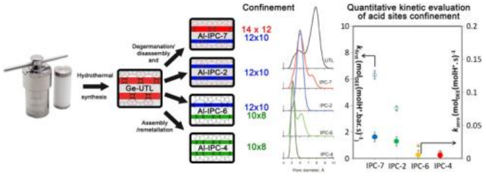
Abstract Text: The relationship between the chemical composition and the activity of zeolites has been unambiguously established and used to optimize some reactions.[1] However, the relationship between the location of acid sites in different micropores and the activity of zeolite catalysts remained elusive, mostly because the available synthetic methods precluded variations in zeolite pore structure without affecting local framework geometry. Recently, the application of Assembly-Disassembly-Organisation-Reassembly (ADOR) protocol to the UTL germanosilicate made it possible to design so-called isoreticular zeolites IPC-n (n = 2, 4, 6, 7), featuring the same topology, but different micropore sizes (Image 1, left).[2]

In this work, we combined the ADOR strategy and isomorphous substitution to produce Al-containing UTL-derived isoreticular zeolites with similar framework chemical composition, concentration of Brønsted acid sites and crystal size. The targeted characteristics of the catalysts were verified using a combination of XRD, Ar physisorption, solid state NMR and FTIR spectroscopies of co-adsorbed probe molecules of variable sizes. The kinetic study of gas-phase ethanol-to-diethyl ether conversion, a quantitative probe for the confinement of acid sites, confirmed Al-substituted isoreticular zeolites as useful model catalysts for studying the pore size effect on catalytic performance. In particular, much lower values of rate constants for the bimolecular dehydration pathway (kfirst) in Al-IPC-6&Al-IPC-4 vs. Al-IPC-2&Al-IPC-7 (Image 1, right) match the expected results from the predictive analysis of the structure−function relationship between Al siting and resulting kinetics.

Thus, the use of Al−IPC-n zeolites as model catalysts can shed a light on the fundamental structure−activity relationship in important acid-catalyzed reactions and help to optimize the relevant processes.

Image 1:



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New Synthetic Methods and Post-Synthetic Modification|Zeolites/Inorganic materials

FEZA21-OR-075

Fine-tuning the molecular sieving properties of aluminosilicate zeolites by post-synthesis functionalization of the interior surface for light olefin/paraffin separation

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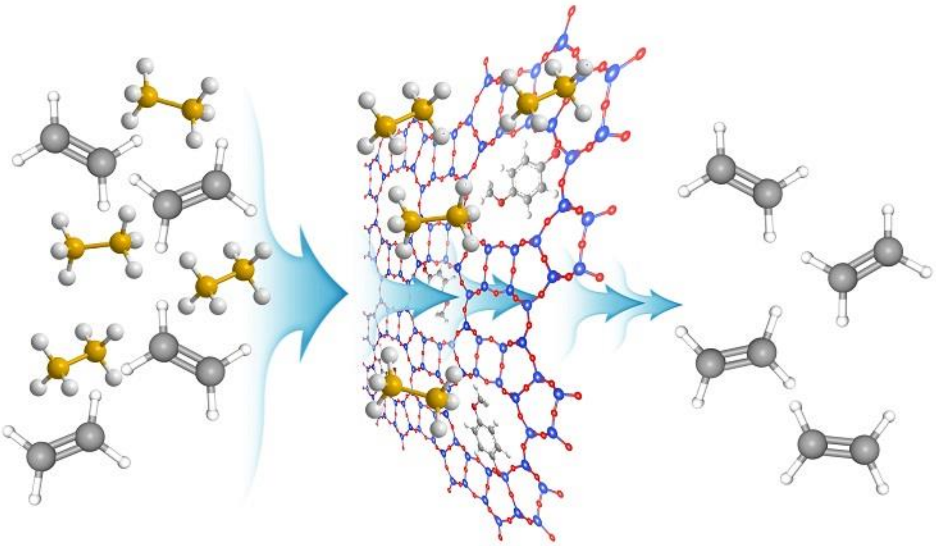
Abstract Text: There are great challenges in developing tailor-made adsorbents to replace the currently used cryogenic distillation processes for light olefin/paraffin separation, due to similar physical properties of the two molecules[1]. The current technique for the discovery of efficient adsorbents is based on the bottom-up construction into a nanoporous structure (*e.g.* zeolite, metal-organic frameworks[2]), which can selectively adsorb a specific target molecule. However, such a strategy is extremely difficult when applying for the light olefin/paraffin separation with a very small molecular dimension. Therefore, there are very few molecular sieving materials that can separate the olefin/paraffin mixture with high selectivity.

Herein, we show that molecular sieving properties of pre-formed aluminosilicate zeolites can be finely tailored by post-synthesis functionalization. The post-synthetic functionalization involves the covalent attachment of the organic moiety (methoxybenzene, methylbenzene, benzene, *etc*) onto the framework bridging oxygen *via* C-$O_{zeolite}$ bond formation, which was proved by Rietveld refinement analysis of XRD, NMR, and IR spectroscopy. 4-methoxybenzene-functionalized MOR separated ethylene from ethane with an ideal-adsorbed-solution-theory selectivity of ~5873, whereas toluene-grafted MOR completely separated propylene/propane mixtures.

In addition to tailoring the molecular sieving property, the micropore environment can be changed by attachment of various functional groups, such as OH, COOH, NH_2 onto micropore walls. We demonstrate that the engineering micropore environment of post-synthetic modification can be used to efficiently screen for a suitable pore environment for use as CO_2 adsorbents under humid conditions.

Image 1:



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New Synthetic Methods and Post-Synthetic Modification|Zeolites/Inorganic materials

FEZA21-OR-076

DEVELOPMENT OF ZEOLITE/POLYMER BASED COMPOSITE VIA PHOTOPOLYMERIZATION AND APPLICATION IN THE FIELDS OF 3D PRINTING AND ADSORPTION

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Abstract Text: Zeolites are a set of crystalline aluminosilicates with a large amount of microporous structures, the large specific surface area and good adsorption. [1] Therefore, zeolites have been widely used in different applications, such as petrochemical industry, environmental protection and biological engineering. However, the direct utilization of powdery zeolites in chemical operation leads to a massive loss of raw materials and equipment contamination, which increases the cost in industrial applications. Therefore, zeolites are normally manufactured into various shapes to meet different industrial demands, such as pellets, beads, etc. Additive manufacturing (AM), as known as 3D printing, brings convenient, cheap, and promising opportunities to fabricate zeolite monoliths with adapted shape and size. [2] 3D printing *via* photopolymerization is developing rapidly and has been a turning point of additive manufacturing (AM), due to its mid reaction conditions, nearly no release of volatile organic compounds (VOCs), etc. In addition, zeolite also can be used as filler to improve or enhance the mechanical properties and functions of polymers. However, works have been rarely reported about the 3D printing *via* photopolymerization of zeolite/polymer, which can be applied to fabricate zeolite monoliths with bespoke shapes and manufacture functional composites. [3]

Here, we report the fabrication of zeolite/polymer based composite *via* photopolymerization (Images 1 and 2). The results show that the zeolite filler content of this composite can reach at least 70 wt%, with good depth of cure and improved mechanical properties. Through SEM analysis, zeolites have a homogenous distribution in the composites, which provides a guarantee for the future 3D printing and fabrication of zeolite with bespoke structures. Although the issue of light penetration in filled samples is unavoidable, the production of 3D patterns can be performed through direct laser writing (DLW) as a lithography technique. Remarkably, a high zeolite porosity can be obtained with the 3D-printed structure, after debinding of the 3D-printed composite by thermal treatment. Compared with the corresponding pure zeolite powder, the porosity is only slightly reduced, which means these materials can be applied in field of adsorption and separation.

In conclusion, this work is expected to promote the valuable development of highly filled zeolite/polymer composites, and expand their potential application for 3D printing *via* photopolymerization in the field of high-performance lightweight materials, such as the fabrication of zeolitic objects with bespoke shapes for adsorption and separation.

Image 1 : The depth of cure (DOC) and the dynamic thermomechanical analysis (DMA) of PEGDA/LTA-5A based composite with different filler contents;

Image 2 : N_2 adsorption-desorption of LTA-5A powder (after 600 ^oC treatment) and PEGDA based composite with 75 wt% LTA-5A after sintering at 600 ^oC.

Image 1:

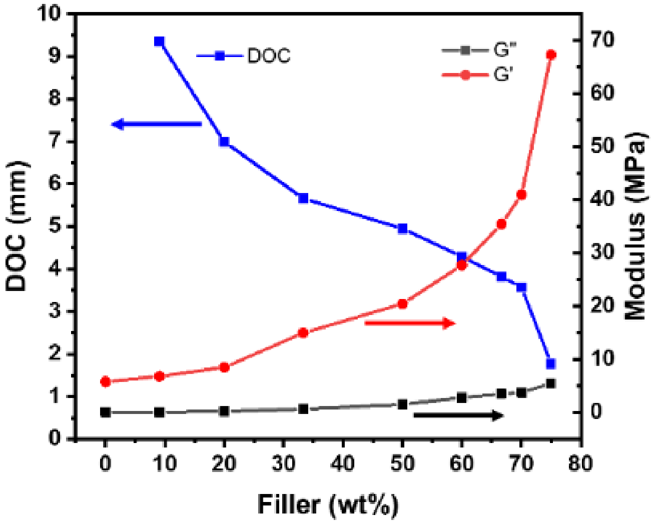
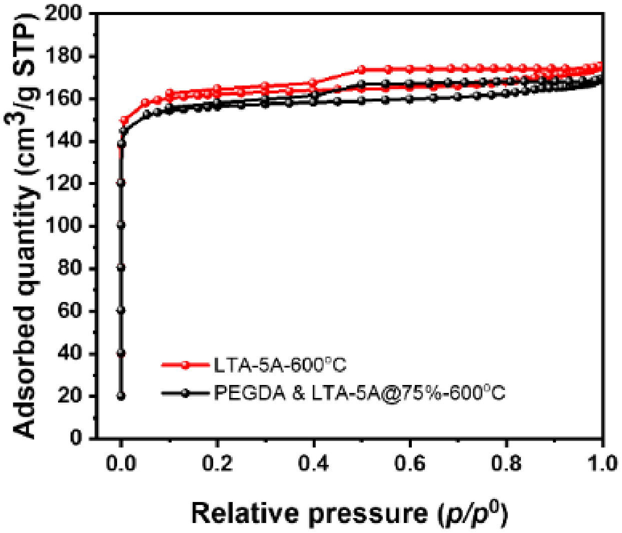


Image 2:



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New Synthetic Methods and Post-Synthetic Modification|Zeolites/Inorganic materials

FEZA21-OR-077

Multivalent Cations Function as Accelerants and Structure-directing Agents of Zeolite Crystallization

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Abstract Text: Multivalent Cations Function as Accelerants and Structure-directing Agents of Zeolite Crystallization

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Zeolites are nanoporous aluminosilicates widely used as commercial adsorbents, heterogeneous catalysts, and ion-exchange materials due to their unique porosity, acidity, and (hydro)thermal stability. There are currently over 245 known zeolite framework types, and the vast majority of these structures are prepared synthetically under hydrothermal conditions in alkaline media, and often in the presence of an organic structure-directing agent (OSDA) that directs the assembly of diverse porous networks. Due to economic and environmental disadvantages of OSDAs, it is often more desirable to synthesize zeolites in the absence of organics; however, less than 15% of zeolite structures have been reportedly synthesized in OSDA-free media. Among these cases, alkali metals are most commonly employed as inorganic structure-directing agents. Many zeolites derived solely from alkali metals are usually prepared under moderate conditions using temperatures less than 100 °C and synthesis times on the order of hours.[1] One notable exception is zeolite chabazite (CHA framework), which is prepared from potassium ions and requires atypically long crystallization times on the order of weeks. Shortened synthesis times require alternative approaches, such as the use of zeolite crystal seeds. In this presentation, we will summarize our studies of zeolite synthesis where alkali metals are partially replaced by multivalent ions. Examples include chabazite synthesis from growth solutions prepared with potassium and small quantities of strontium. Our findings reveal that these conditions yield fully crystalline chabazite within hours without the need for either organics or crystal seeds.[2] Similar studies of strontium inclusion in seed-assisted syntheses also reveal shorter crystallization times. Notably, we show that strontium has a pronounced impact on the kinetics of chabazite formation, leading to 14- and 3-fold reductions in crystallization time compared to pure potassium syntheses in the absence and presence of crystal seeds, respectively. Using a combination of ^{29}Si and ^{27}Al MAS NMR spectroscopy, we also show that strontium functions as a structure-directing agent based on its ability to alter Q^4(nAl)^{29}Si speciation, thereby redistributing tetrahedral Al sites in the framework. Given the widespread application of chabazite in adsorption and separation processes, designing facile and efficient synthesis approaches with concomitant control of physicochemical properties is commercially relevant. Details of these studies along with other analyses of multivalent/alkali metal combinations will be discussed in this presentation.

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New Synthetic Methods and Post-Synthetic Modification|Zeolites/Inorganic materials

FEZA21-OR-078

Isomerization of unsaturated fatty acids with hierarchical ZSM-5

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Abstract Text: Branched fatty acids, usually isostearic acids, are of great interest for the oleochemical industry due to their interesting physicochemical properties.[1,2] Isostearic acid is industrially produced as a side product of the clay catalyzed dimerization of unsaturated fatty acids. The yield of isostearic acid is low, and multiple, energy consuming, purification steps are necessary to obtain a pure fraction of isostearic acid.[3] Current research therefore focusses on the use of zeolites as catalysts for the production of branched fatty acids in the so called isomerization of unsaturated fatty acids to unsaturated branched chain fatty acids. The use of zeolites is advantageous compared to the use of clays, and this thanks to their mainly microporous character. As such, branched fatty acids are formed more selectively and the formation of unwanted oligomeric side products is retarded. Different zeolite topologies have already been used successfully for the production of branched fatty acids. Today, the best results in literature are obtained with FER, with which yields more than 70 % can be achieved. However, this is in the presence of different additives.[4]

Our research group has recently shown that also with other zeolite topologies it is possible to develop high performing catalytic systems for the isomerization of unsaturated fatty acids to unsaturated branched chain fatty acids. Moreover, we were able to obtain high yields of branched fatty acids comparable to those obtained with FER without the use of any additives.[5] To do so, we used a hierarchical zeolite, i.e. a zeolite which contains on top of and interconnected with its micropores, also mesopores. These hierarchical zeolites can be both obtained via top-down methods, i.e. via post-synthetic treatments using acids and/or bases, or via bottom-up methods where the mesoporosity is built in during synthesis.[6] By using a combination of post-synthetic treatments on the economically more interesting MFI zeolite, we obtained a very active zeolite which can compete against the current state-of-the-art FER zeolite both with regard to activity and selectivity towards the branched fatty acids, and this without the use of any additives or solvents. Moreover, thanks to a thorough characterization of both the parent MFI material and the hierarchical MFI, we were able to show that the activity of the MFI zeolite in this type of reaction is strongly related to the accessibility of the catalytically active sites, i.e. the Bronsted acid sites. Thanks to the presence of extra mesoporosity in the hierarchical MFI sample, more Bronsted acid sites were made available for catalysis while at the same time, the intracrystalline diffusion is improved.[5]

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Novel Materials and Structural Methods

FEZA21-OR-079

Direct Atomic-Level Imaging of Zeolites by Electron Microscopy: From Oxygen bridges to Extra-framework Light Cations, including Iron Framework Atoms and Bimetallic Compounds

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Abstract Text: There is a continuous effort to design novel materials that display superior performance towards the desired application. In order to finely tuning the physicochemical properties of zeolites and metal loaded zeolites, gaining knowledge at atomic level is crucial to correlate their structural features with their chemical behavior (activity, selectivity and stability). Advanced transmission electron microscopy could retrieve structural information with atomic level[1] (especially after the implementation of the spherical aberration correctors which potentially allow reaching sub-Ängstrom spatial resolution) and it has been the most demanded methodology for the characterization of all kind of inorganic solids. However, for the case of zeolitic frameworks, its application has been diminished due to the severe beam damage that they suffer under the electron irradiation leading into the irreversibly framework disruption within only few seconds. To overcome this difficulty different approaches have been undertaken with the intention of minimizing the beam damage while obtaining the maximum degree of information[2].

A unique advantage of TEM versus other technique is the possibility of gaining local information; herein, all framework atoms, including oxygen bridges and most extra-framework sodium cations were observed in one of most electron-beam-sensitive and lowest framework density zeolites, which is the Na-**LTA**. The data was obtained by using a new imaging mode, using an annular bright field (ABF) detector, which has been found extremely useful for revealing light elements information as well as to extend the spatial resolution. On the other hand, by using an annular dark field (ADF) detector, information of heavier elements than the framework can be acquired. With a careful control of the electron dose and by combining the ABF and ADF data the location of iron atoms, which isostructurally substituted the “T” atoms of the **MFI** framework type, has been determined for the first time[3]. All data obtained was compared and corroborated with image simulations, electron diffraction tomography and theoretical DFT calculations.

In addition, **EMT**, an important framework type due to its large pore opening and low framework density as **FAU**, was also studied at atomic level by advanced imaging techniques and by 3-dimensional electron diffraction[4], observing lead and potassium cations which were both incorporated inside the pores and that were not distributed in an fully periodic manner.

Acknowledgements

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Novel Materials and Structural Methods

FEZA21-OR-080

Exploiting resonant X-ray powder diffraction at the Al K edge to locate aluminum in zeolite frameworks

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Abstract Text: The position of aluminum in a zeolite framework structure defines the accessibility and geometry of the catalytically active sites, so a crystallographic determination of the Si-Al ordering would enable a better understanding and fine-tuning of a zeolite catalyst. However, there is currently no general method that can identify directly which T sites in a zeolite framework structure are occupied by aluminium. Recognizing T-site dependent reactivity of zeolites is a long-standing question in zeolite science that to date remains unanswered, because the aluminum substitution for silicon is usually only partial (typical zeolite catalysts have Si:Al ratios larger than 5) and the scattering power of these two elements is very similar.

To address this problem, we have exploited the properties of resonant (anomalous) X-ray powder diffraction (AXRD) across the Al K edge (1.56 keV), where the aluminum scattering factor changes drastically while that of silicon remains unchanged. Those changes in the scattering power highlight aluminum in the structure. While the well-established X-ray absorption methods exploited at the Al edge are short-range probes and can report only on local environment around the aluminum position, AXRD can collect information of the long-range structural order of Al:Si distribution and consequently unambiguously pinpoint aluminum's position in the framework. Because the diffraction limit at 1.56 keV corresponds to a *d* spacing of only 3.98 Å, the data from a conventional measurement were combined with those at energies near the X-ray absorption edge to quantify the aluminum concentration at all T sites in the refined zeolite structure.

In this way, two **FER**-type zeolites with identical chemical compositions but the different distributions of aluminum and different catalytic properties could be determined quantitatively and unambiguously. One sample was more active and selective in the isomerization of *n*-butene to *i*-butene than the other, but it also deactivated much faster.[1,2] This could be better understood from the aluminum ordering found. The higher activity and faster deactivation was due to the higher proportion of active sites in the accessible 10-ring channels. The results are in line with previous studies performed on the same samples, but are also quantitative.

These analyses demonstrate that the method can be applied even for zeolites with Si:Al ratios as high as 15. The method yields a quantitative characterization of the catalytically active sites in a zeolitic material, and that, in turn, allows the activity of that zeolite to be understood and fine-tuned. This constitutes a major advance in our fundamental understanding of the relationship between zeolite structure and catalytic activity. We believe that AXPD at the Al K edge could become the technique of choice for zeolite scientists interested in locating the active catalytic sites in their materials.

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Novel Materials and Structural Methods|Zeolites/Inorganic materials

FEZA21-OR-081

Hydrothermal Transformation of Diatoms into Zeolite Chabazite-Diatom Composite and Testing in Ammonia -Selective Catalytic Reduction (SCR) Applications

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Abstract Text:

1. Introduction

Diatoms are hierarchically organized, porous (micro-, meso- and macro size range) materials with a wide variety of structures and shapes having SiO_2 content mostly more than 90 wt.%. In general, they are used in water filtration, as pet litter, as abrasives etc. [1]. In recent years, there has been renewed interest in using diatoms as silica sources as well as coated or reactive supports for the synthesis of industrially important zeolites, such as MFI [2], BEA [3] and FAU [4]. We have recently reported a chabazite-type (CHA) zeolite composite material (CHA-diatom) that comprises a favourable combination of both microporous (CHA) and macroporous (diatom) characteristics [5], for use in NH_3-SCR reaction. For the first time, we report here our detailed characterization of CHA-diatom composite by various physico-chemical techniques, such as X-Ray Diffraction (XRD), Scanning Electron Microscopy/Energy Dispersive X-ray spectroscopy (SEM/EDX), Thermogravimetry-Differential Thermal Analysis (TG-DTA), Magic Angle Spinning-Nuclear Magnetic Resonance spectroscopy (MAS-NMR), N_2-sorption and Hg-porosimetry measurements; and catalytic test results.

2. Experimental

Hydrothermal transformation of diatom into CHA-diatom composite was carried out under hydrothermal conditions using 1-adamantyltrimethyl-ammonium hydroxide (25% aqu.) as the template and sodium aluminate (20.0 wt.% Al_2O_3 and 19.3 wt.% Na_2O) as the additional aluminium source [5]. No other conventional silica source was used for the hydrothermal transformation of diatom. Composites having different amounts of zeolite content were synthesized by adjusting the synthesis parameters [5]. The H-forms of CHA-diatom composites were prepared and ion-exchanged with copper (Cu)-nitrate solution via wet impregnation procedure to test in NH_3-SCR reaction under the conditions generally prevalent for automotive emission treatment systems.

3. Results and Discussion

Fig. 1 shows the XRD patterns of the starting diatom and the CHA-diatom composites having different Si/Al ratios obtained via hydrothermal transformation of diatoms. It should be noted that a minor undesired impurity phase (cristobalite) is present in diatom. Nevertheless, the XRD patterns of the composites with different Si/Al ratios matches well with the XRD pattern reported for CHA-type zeolite. SEM images (Fig. 2) of the diatom and CHA-diatom indicate that the basic macroporous morphology of diatom is retained during the hydrothermal transformation process. EDX measurements and elemental mappings of CHA-diatom (not shown here) indicate that aluminium is uniformly distributed over the diatom matrix, thereby providing indirect evidence on the homogeneous distribution of zeolite CHA-type structural fragments over the diatom matrix. The physico-chemical characteristics of the composites having different zeolite contents are summarized in Table 1.

4. Conclusions

In conclusion, partial transformation of diatoms into CHA/diatom composites was achieved under hydrothermal conditions. The zeolite content was adjustable up to 60% without losing the macroporous character of the diatoms. Preliminary catalytic tests reveal that the Cu-containing CHA-diatom composites are catalytically active for the NH_3-SCR reaction, which will be presented in detail.

Image 1:

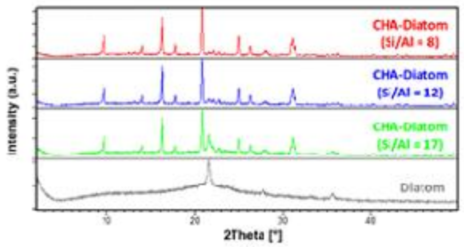
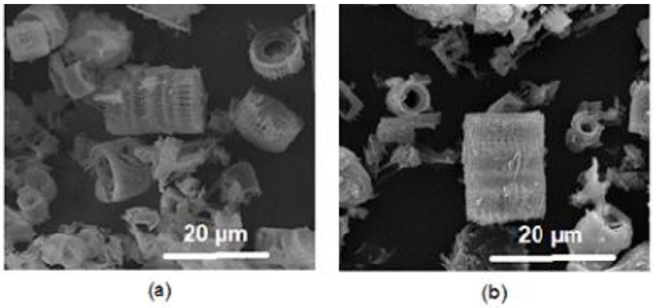


Fig. 1 XRD patterns of diatom and CHA-diatom composites with different Si/Al ratios.



(a) (b)

Fig. 2 SEM images of: (a) Diatom and (b) CHA-diatom composite (Si/Al = 13).

Image 2:

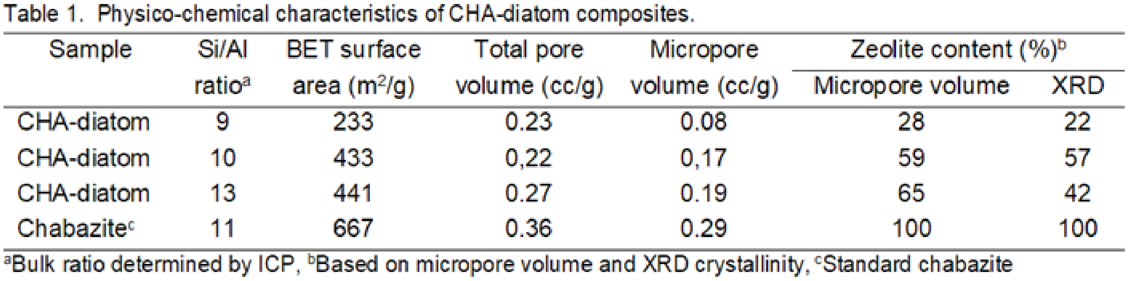


Table 1. Physico-chemical characteristics of CHA-diatom composites.

Sample	Si/Al ratio^a	BET surface area (m^2/g)	Total pore volume (cc/g)	Micropore volume (cc/g)	Zeolite content (%)^b	
					Micropore volume	XRD
CHA-diatom	9	233	0.23	0.08	28	22
CHA-diatom	10	433	0,22	0,17	59	57
CHA-diatom	13	441	0.27	0.19	65	42
Chabazite^c	11	667	0.36	0.29	100	100

^{a}Bulk ratio determined by ICP, ^{b}Based on micropore volume and XRD crystallinity, ^{c}Standard chabazite

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Novel Materials and Structural Methods|Zeolites/Inorganic materials

FEZA21-OR-082

Disorder in non-cage Containing Zeolites

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Abstract Text: Zeolites are often synthesized as small polycrystalline powders that make their structure determination by single crystal X-ray diffraction challenging. 3D electron diffraction (3D ED) methods[1], especially continuous rotation electron diffraction (cRED)[2], overcome the size limitation and can reveal structures of sub-micrometer sized crystals with similar resolution as single crystal X-ray diffraction.[2] In this work, we have utilized cRED to reveal unprecedented disordered chains that link together the *non* cages $[4^15^8]$ in nonasil (NON)[3] to form its complete 3D framework. The refinement against the cRED data in the reported *Fmmm* space group revealed residual peaks in the electrostatic potential maps that clearly indicate two configurations of the zig-zag chains that link the *non* cages together. These atoms reside on a mirror plane perpendicular to the c-axis. Another mirror plane that is perpendicular to the b-axis prevents them from relaxing into either configuration, and replacing it with a two-fold rotation axis allows full relaxation. Hence, the structure is best described by superposition of two *Fm*2*m* models, or two 50% occupant chain configurations in *Fmmm*. Herein, with cRED and computational aid, we uncover the origin of the disorder and demonstrate that the same disorder is prevalent in all *non*-cage containing zeolite structures CIT-13 (*CTH), ERS-18 (EEI), EMM-25, EU-1 (EUO), ITQ-27 (IWV), and NU-87 (NES), except for ITQ-32 (IHW) and IM-12 (UTL).[4]

Image 1:

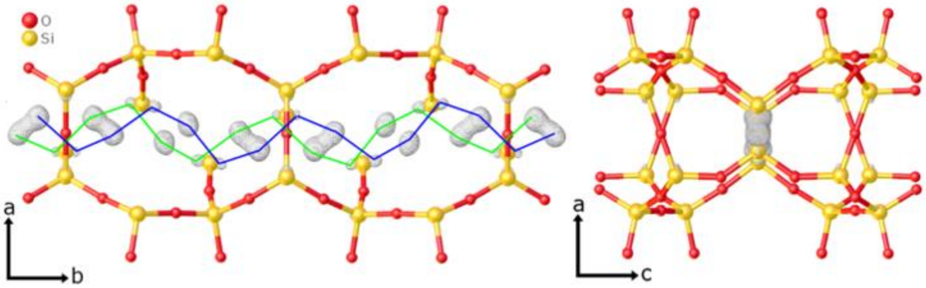

Figure 1. Difference Coulomb potential maps of nonasil refined in *Fmmm* space group at 0.5 e⁻/Å level clearly depicting two possible chain configurations distinguished in green and blue.

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Novel Materials and Structural Methods|Zeolites/Inorganic materials

FEZA21-OR-083

PST-33: THE LAST MEMBER OF THE 4-LAYER ABC-6 FAMILY OF ZEOLITES

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Abstract Text: While zeolites and related microporous materials are an important class of industrial catalysts and adsorbents, much attention has been devoted to the discovery of novel small-pore zeolites over the past decade. This is probably due to the successful commercialization of SSZ-13 and SAPO-34, the aluminosilicate and silicoaluminophosphate (SAPO) versions of CHA-type zeolites as a catalyst support for the selective catalytic reduction of NO_x with NH_3 and as a catalyst itself for the methanol-to-olefins reaction, respectively. CHA-type zeolites belong to the ABC-6 family of framework structures, consisting layers of hexagonally arranged 6-rings stacked in different sequences. There are also three possible positions for the lateral translation of the layers, denoted as A, B, and C, like the packing of spheres, leading to an almost infinite number of framework structures: the framework type CHA has the stacking sequence AABBCC.

The ABC-6 family of zeolites when constructed from no more than four different types of cages starts from the 2-layer stacking sequence AB which was observed in cancrinite (CAN). This is followed by offretite (OFF) and sodalite (SOD) with two 3-layer framework structures with stacking sequences AAB and ABC, respectively. On the other hand, there are three possible 4-layer framework structures. Two of them were already found in gmelinite (GME) and losod (LOS) with stacking sequences AABB and ABAC, respectively. However, the last one with the stacking sequence AABC has never been observed so far. Here, we present the synthesis of this missing member of the 4-layer ABC-6 family of zeolites, denoted PST-33, using a certain organic structure-directing agent (OSDA) via multiple inorganic cation approach. The structure of PST-33, which contains 14-hedral ($[4^6 6^8]$) *sod* and 17-hedral ($[4^9 6^5 8^3]$) *lev* cages, as well as smaller 8-hedral ($[4^6 6^2]$) double 6-rings (*d6rs*), has been solved by synchrotron single-crystal X-ray diffraction (XRD). We will also report the CO_2 adsorption properties of its various alkali cation forms.

Novel Materials and Structural Methods|Zeolites/Inorganic materials

FEZA21-OR-084

Extracting the synthesis–structure relationship hidden behind the elaborate synthesis of zeolites by a data-driven approach

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Abstract Text: Data-driven approaches, including applications of machine learning, have expanded to solve not only problems in materials science but also other human-level problems. This machine learning-based approach enables us to extract the most significant synthesis descriptors from chemical space with a high dimension and massive entries, which is sometimes very hard to be handled by humans.

The empirical nature of the current understanding of zeolite synthesis stems from the difficulty in correlating synthesis conditions and their consequences for materials formed as metastable phases via kinetically controlled pathways[1–3]. Effective descriptors that can link synthesis conditions and products are thus very important to rationalize historical experiments as well as to predict novel synthesis conditions. We trained extreme gradient boosting (XGBoost), one of the supervised machine learning techniques, against 686 organic structure-directing agent (OSDA)-free zeolite syntheses collected from the literature to predict crystallized zeolites from synthesis conditions. The decision tree generated from the trained model by XGBoost showed that Na/(Si+Al) and Si/Al were more significant than the other synthesis descriptors (Fig. 1). Detailed analysis of the decision tree and literature data revealed that structural similarity in zeolite structures is pronounced in synthesis conditions that satisfy $Na/(Si+Al) \leq 0.57$ and $Si/Al > 5.0$. This range is consistent with conditions that have realized seed-direct, OSDA-free synthesis of zeolites where structural similarity is a key for the working hypothesis[4]. In addition, the significant structure descriptors were identified based on the importance of the synthesis descriptors by XGBoost. Further, we constructed a structural similarity network from XGBoost (Fig. 2). In this similarity network, the clustering algorithm identified seven communities, which were colored and labeled as communities (i)–(vii). In these communities, community (vi) is used to predict a novel synthesis condition using OSDA for EUO-type zeolite[5].

The knowledge extracted from the machine learning models rationalized physicochemical, structural, and empirical insights into the zeolite chemistry. Therefore, the guided synthesis of zeolites based on the synthesis–structure relationship can be used to not only rationalize the known syntheses and discover novel zeolites but also to increase the size and diversity of the available datasets, which are remarkably important for improving the linkages between synthesis descriptors and structure descriptors. It is anticipated that our approach presented here is not limited to zeolites and hence can be applied to all classes of materials.

Acknowledgements

The computational resources were provided by the Supercomputer Center in Institute for Solid State Physics (ISSP) of The University of Tokyo and Research Center for Computational Science at the Institute for Molecular Science (IMS) in Okazaki, Japan.

Image 1:

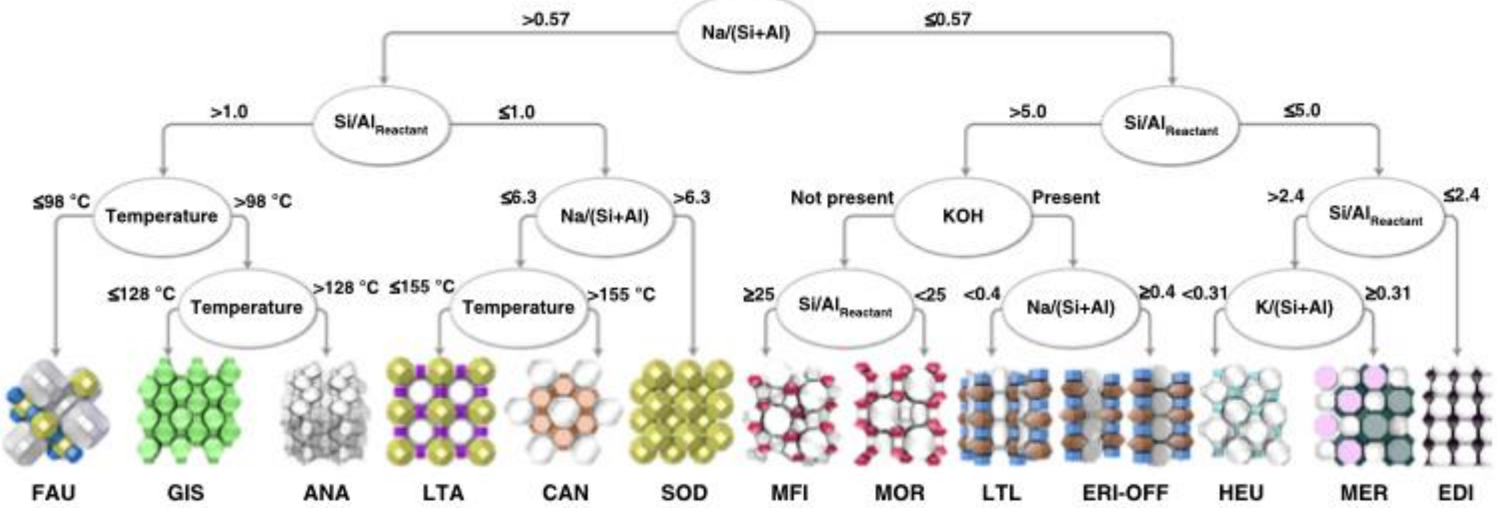

Fig. 1 Decision tree constructed from the trained model with the highest accuracy of the XGBoost. In OSDA-free synthesis of zeolites, the most significant synthesis descriptors for zeolite phase selection are the amounts of SiO_2, Al_2O_3, MOH (M = Li, Na, K, etc.), and H_2O present in the synthesis mixture.

Image 2:

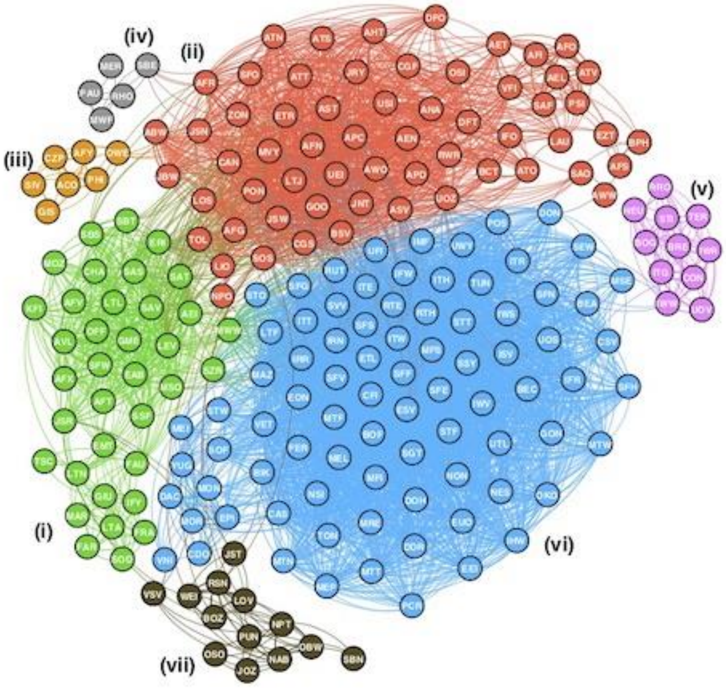

Fig. 2 Similarity network for the zeolite structures. The layout of the network is decided by a force-directed algorithm. Communities are identified using a clustering algorithm based on the modularity optimization.

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Novel Materials and Structural Methods|Zeolites/Inorganic materials

FEZA21-OR-086

Spectroscopic evidence on the changes in the F-Si bonding and the local structure of silicon atoms in highly crystalline pure silica RTH-type zeolite

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Abstract Text: In recent years, a new family of OSDAs based on tetraalkylphosphonium and phosphacenes cations have been employed and attracted much attention providing new opportunities for the new synthesis of zeolites. [1] The P-containing are advantageous against the N-containing OSDAs because its higher thermal stability allows increasing the temperature of synthesis. In the presence of fluoride, the higher positive charge centered in the P atom favours the electrostatic OSDA$^+$-F$^-$ interaction in the solid leading to highly crystalline and well-ordered zeolites. [2] Moreover, the higher electronic density over the P atom facilitates the localization of the OSDA inside the zeolite by X-Ray diffraction, and the ^{31}P (I = ½, 100% abundant) is more suitable than ^{15}N nuclei (I = ½ and 0.36% abundant) for Nuclear Magnetic Resonance (NMR) studies. The use of this new family of P-containing OSDAs has allowed the synthesis of a wide number of known zeolites and novel zeolite structures such as ITQ-26, ITQ-27, ITQ34, ITQ-45, ITQ-47, ITQ-49, ITQ-52, ITQ-53 and ITQ-58. [1]

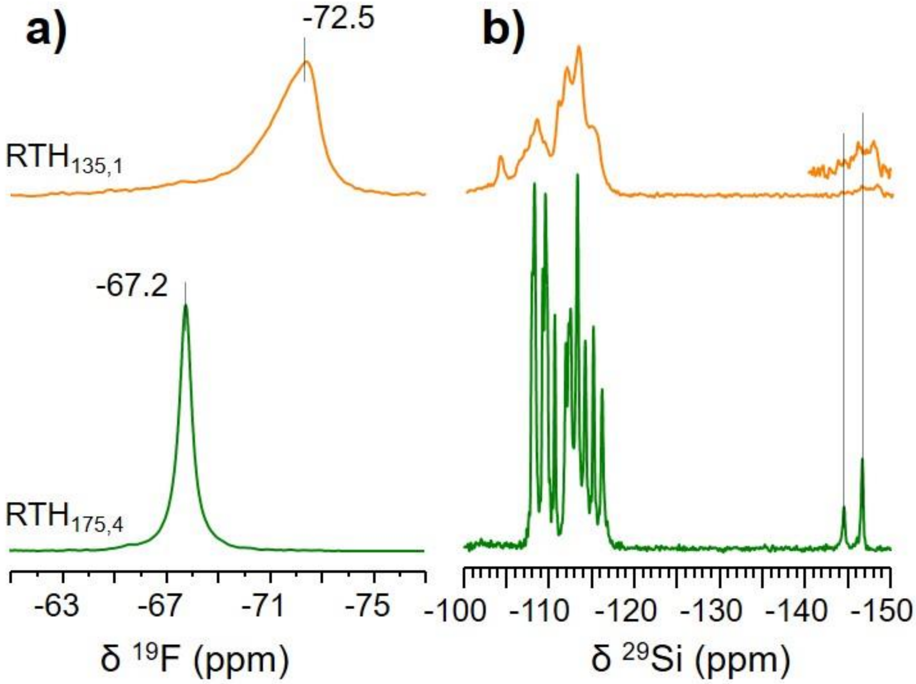
Here, we report the synthesis of pure silica RTH-type zeolite in fluoride media using tri-isopropyl-methyl-phosphonium (TIPMP) as OSDA from gels of composition $1SiO_2 : 0.4ADE^+OH^- : 5H_2O : 0.4$ HF, under stirring at different temperatures: 135 °C, 150 °C and 175°C. The obtained samples are called RTH$_{X,Y}$, where X denotes the temperature and Y refers the synthesis time in weeks. The resulting four zeolites were deeply characterized mainly using solid state NMR in combination with high resolution XRD [3] and theoretical calculations.

The XRD patterns of the four samples are typical of highly crystalline RTH-type zeolite and show only weak differences in the position of some peaks. The four RTH samples show similar ^{13}C, ^{31}P and ^{1}H MAS NMR spectra, consistent with the incorporation of the TIPMP molecules with similar conformation within the zeolite voids. However, significant differences are observed in the ^{19}F and ^{29}Si NMR spectra, as shown in **Figure 1**. The ^{19}F NMR spectra of the RTH$_{135,1}$ and RTH$_{175,2}$ zeolites show signals at *d* ^{19}F =-72 ppm and *d* ^{19}F =-67 ppm respectively, of ^{19}F in the *rth* units. The ^{29}Si NMR spectrum of zeolite RTH$_{175,4}$ is highly resolved being distinguishable 16 peaks including penta-coordinated Si, indicating that the zeolite contain at least 16 crystallographic sites. [3] Meanwhile, the spectrum of zeolite RTH$_{135,2}$ show broader signals and a characteristic peak at *d* ^{29}Si =-104 ppm. Therefore, the NMR spectra indicates relevant differences in the local structural order of the RTH zeolite depending on the synthesis conditions. High resolution powder XRD allowed determining the exact position of the OSDA in the RTH$_{175,4}$ zeolite, which has been used to optimize the RTH structure and localize the ^{19}F atom at PBE level of theory (Perdew–Burke–Ernzerhof generalised gradient approximation). The atomic positions and the cell parameters were allowed to relax in all geometry optimizations, and NMR absolute shielding values were calculated employing the gauge included projector augmented wave (GIPAW) formalism implemented in VASP. Comparison with the experimental results allowed to identify the exact position of the ^{19}F inside the *rth* cage of the zeolite.

The evolution of the ^{19}F and ^{29}Si NMR signals suggest that the position of the fluorine atoms change with the synthesis conditions, leading to highly crystalline RTH crystals with higher uniform short range order TO$_4$ positions at high temperature and long crystallization time. The combination of NMR, powder XRD and DFT calculations is a powerful way to determine the complete structure of the as-made zeolites when obtaining large single crystals of the zeolites is not possible.

Figure 1. MAS-NMR spectra of RTH$_{135,1}$ and RTH$_{175,4}$ zeolites, a) ^{19}F and b) ^{29}Si.

Image 1:



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Novel Materials and Structural Methods|Zeolites/Inorganic materials

FEZA21-OR-087

Synthesis and Characterization of Novel Small-Pore (Silico)Aluminophosphates

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Abstract Text:

Microporous materials are at the heart of many commercial processes, particularly in the fields of catalysis, adsorbents, and separations. In industry, these materials, also called molecular sieves, have traditionally been synthetic aluminosilicates (i.e., synthetic zeolites) as well as their phosphate-based analogues, the aluminophosphates (AlPOs) and silicoaluminophosphates (SAPOs). Small-pore molecular sieves in particular are widely employed in a variety of industrial areas. For example, the 8-ring LTA zeotype is found in numerous adsorbent and separation applications, such as air separation by pressure swing adsorption. In catalysis, SAPO-34 is the material of choice for the conversion of methanol to light olefins (MTO reaction), while copper-containing CHA zeolites can be found in many selective catalytic reduction (SCR) catalysts for the conversion of nitrogen oxides to ammonia.

Many of these small-pore molecular sieves are members of the ABC-6 family of zeotypes. This class of porous materials is composed of 6-membered rings of tetrahedral atoms (linked by bridging oxygens), which are stacked along the c-axis of a hexagonal unit cell. The 6-rings can assume one of three positions in the unit cell, commonly designated as A, B, and C. The connectivity and ordering of the A, B, and C positions determines the proportions of double-6-ring (*d6r*) and single-6-ring (*s6r*) subunits in the material, which in turn affect the secondary/composite building units and ultimately the overall porosity.

The ABC-6 family is a very fertile ground for the discovery of new materials. High-throughput computational methods have recently been developed that allow for the enumeration of hundreds of potential novel and interesting structures. In recent years, some of these hypothetical structures have been synthetically realized in either zeolitic or SAPO/MeAPSO form. We recently reported a new ABC-6 aluminophosphate, AlPO-78, which was assigned the structure code **AVE** in 2019. AlPO-78 is a rather remarkable material in many aspects. First, it has the longest reported repeat unit (24 layers) for a synthetic ABC-6 material. Second, it contains a novel cage that was one of the simplest cages predicted to exist by computational methods, but that had not been experimentally realized until our publication. Finally, AlPO-78 is interesting in that it is an ABC-6 material that has an equal number of *s6r* and *d6r* units in its stacking pattern. Such a situation can only exist in ABC-6 materials with 4n (n = 1, 2, 3, etc.) layers in their repeat unit; to our knowledge, STA-2 (**SAT** zeotype) is the only ABC-6 material besides AlPO-78 that possesses this property. This presentation will focus on the structure solution of AlPO-78, as well as several new materials that have been synthesized from modifications of the AlPO-78 synthesis. A brief survey of potential applications of the new AlPO materials will also be presented.

Novel Materials and Structural Methods|Zeolites/Inorganic materials

FEZA21-OR-089

Reactive Neural Network Potentials for Zeolites with Density Functional Theory Accuracy

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Abstract Text: Machine learning interatomic potentials (MLPs) are becoming increasingly popular in multiple areas of material science, focusing on determination of material structure, chemical reaction dynamics or transport processes at the interfaces [1]. The reason for the success of MLPs is their ability to reach *ab initio* accuracy at a cost of the standard reactive force fields such as ReaxFF [2] using established and robust training and data curation procedures. However, vast majority of the studies focus on systems with rather low-dimensional configurational space such as simple metals, binary alloys, a single chemical reaction, non-reactive interaction of a solvent with a simple surface (metallic, alloy or simple oxide) or some combination of the above [1]. This apparent *curse of dimensionality* could be behind the fact that MLPs for nanoporous solids such as metal organic frameworks or even zeolites are, to our best knowledge, basically non-existent [3].

Therefore, in this work, we present the development of the *linear scaling reactive* MLPs for various classes of zeolites. Our MLPs are *neural-network-based* using the *SchNet* architecture [4] with a trainable environment representation that can seamlessly incorporate multiple atom types and that has been shown to provide high accuracy and high data efficiency [5]. We generated a large, curated library (few hundred thousand structures) of density functional theory (DFT) energetic and force data for silicious materials [6], germanosilicates, aluminosilicates zeolites with water and, in addition, for silicious materials with platinum clusters. The library was created by a strategy [6] that attempts to optimally cover the important parts of the configurational space including not only structures close to equilibria but also non-equilibrium structures necessary for description of bond-breaking events, making our neural network potentials (NNPs) truly reactive. The resulting NNPs are able to retain the accuracy of DFT calculations across the complex zeolitic classes considered (Figure 1), e.g., outperforming specialized ReaxFF for silica by order(s) of magnitude in accuracy (Figs. 1a-b), while speeding up the calculations in comparison to DFT by at least three orders of magnitude.

Using the newly developed NNPs we have been already witnessing intriguing (preliminary) results such as: i) revision of the Deem zeolite database (330 thousand hypothetical zeolites) revealing more than 20 thousand additional hypothetical frameworks in the thermodynamically accessible range for zeolite synthesis (Fig 2a) [6]; ii) reactive diffusion and sintering of sub-nanometer Pt clusters in the silicious zeolite [7] associated with intermittent breaking of the windows connecting the zeolite cages (such reactive events were not included in the training database) obtained from multi-nanosecond long molecular dynamics (MD) simulations (Fig 2b); iii) effects of minor topology variations on germanium distribution in germanosilicate zeolites with profound effects on their delamination [8] propensity obtained from comprehensive basin-hopping Monte Carlo runs *(*approx. million points per topology); and iv) complex cooperativity of external surface silanols and silanol nest defects in zeolite desilication under hot pressurized liquid water conditions (obtained from multi-nanosecond long MD runs).

Therefore, our (preliminary) results suggest that with the herein developed accurate reactive zeolitic NNPs we could not only make the dynamical simulations of even the largest zeolitic frameworks under realistic conditions (properly including temperature, pressure, range of heteroatom concentrations or solvent effects) possible, but make it a new standard in the field.

Image 1:

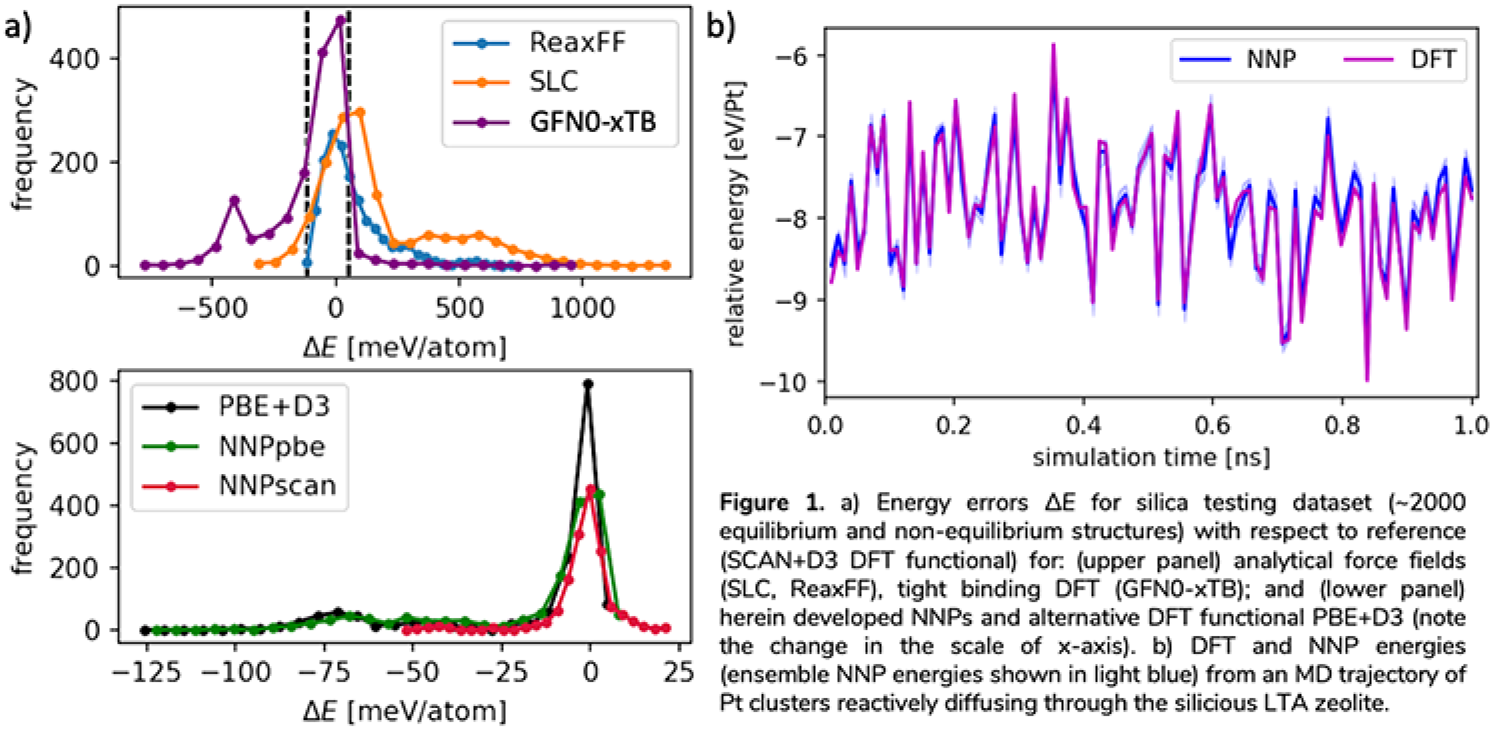

Figure 1. a) Energy errors ΔE for silica testing dataset (~2000 equilibrium and non-equilibrium structures) with respect to reference (SCAN+D3 DFT functional) for: (upper panel) analytical force fields (SLC, ReaxFF), tight binding DFT (GFN0-xTB); and (lower panel) herein developed NNPs and alternative DFT functional PBE+D3 (note the change in the scale of x-axis). b) DFT and NNP energies (ensemble NNP energies shown in light blue) from an MD trajectory of Pt clusters reactively diffusing through the silicious LTA zeolite.

Image 2:

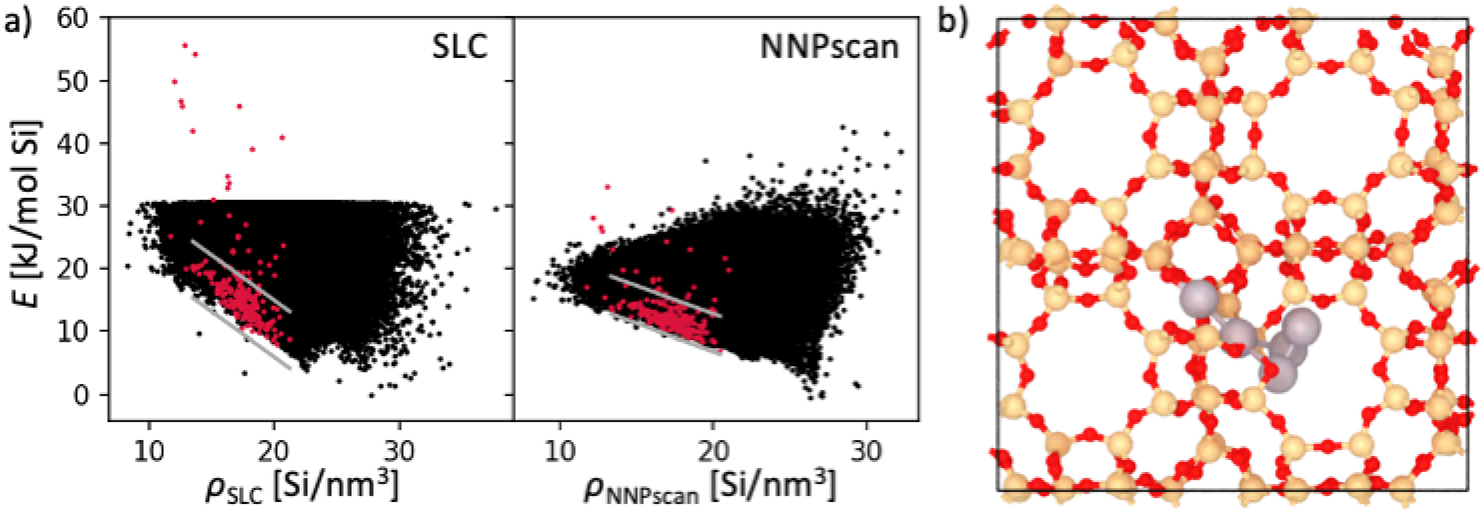

Figure 2. a) The Deem zeolite database plot of relative energies E with respect to α-quartz as a function of framework density ρ of hypothetical (black) and existing (red) zeolites. Solid lines in (a) indicate the energy-density range of purely siliceous zeolites in the TD-accessible range. b) Reactive agglomeration of Pt atom with Pt_4 nanocluster through the window of silicious LTA zeolite.

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Novel Materials and Structural Methods|Zeolites/Inorganic materials

FEZA21-OR-090

Synthesis of microporous titanosiloxane materials using cage siloxane as building blocks

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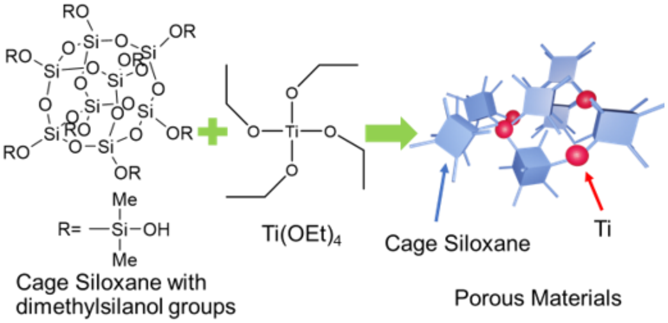
Abstract Text:

Introduction : Siloxane-based nanoporous materials have a wide range of applications.1) Cage siloxanes have attracted much attention as building blocks to construct new porous materials that have not been achieved by conventional synthetic methods of silica-based porous materials such as zeolites.2) In this study, we synthesized microporous titanosiloxane materials with controlled Ti environments by the cross-linking reaction between cage-type siloxane molecules modified with dimethylsilanol groups and titanium tetraethoxide without using any templates or SDAs (Image 1).

Experimental : Cage siloxane with dimethylsilanol groups was reacted with titanium tetraethoxide in a THF solvent at a molar ratio of Si/Ti = 8 under nitrogen atmosphere. Immediately after the addition of titanium ethoxide to a solution of cage siloxane, the white gel-like solids were precipitated. The sample was heated at 40 °C under vacuum condition to evaporate the solvent, and a white powder was obtained. The obtained powder was heat-treated at 250 °C for 1 d in air. To evaluate the catalytic perfomance of the obtained material, liquid-phase oxidation of cyclohexene with tert-butyl hydroperoxide(TBHP) was carried out. In a typical run, 10 mmol of a substrate, 10 mmol of TBHP as an oxidant and 25 mg of a catalyst were mixed and heated to 60 °C for 6 h with vigorous stirring.

Results and Discussion : The powder X-ray diffraction pattern of the products showed a broad peak (d = 1.3 nm). The FT-IR spectrum showed the band assigned to Si–O–Ti vibration at 920 cm^{-1}, indicating the formation of Si–O–Ti bonds by the reaction of SiOH groups and TiOEt groups. Solid-state ^{29}Si MAS NMR analysis confirmed that the signal arising from dimethylsilanol groups (−10 ppm) disappeared and a new signal appeared at −17 ppm. The retention of the cage siloxane unit (−109 ppm) was also confirmed. The ^{13}C CP/MAS NMR spectrum showed no signals due to unreacted ethoxy groups (at 18 ppm and 59 ppm) after the heat treatment. Nitrogen adsorption-desorption isotherms showed that the obtained materials have microporosity before and after heat-treament. The results of the catalytic test for the oxidation of cyclohexene using TBHP showed that a relatively high conversion rate and selectivity were realized. These results indicate the formation of a novel nanoporous material by cross-linking of cage siloxanes with titanium species without using templates.

Image 1:



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Advanced Characterisation and Operando Spectroscopies|MOFs/Organic materials

FEZA21-OR-091

Revealing Structural Details of Nanoporous Materials by Rotation Electron Diffraction Methods

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Abstract Text:

Zeolites and microporous materials have been widely used as absorbents, ion-exchangers, selective catalysts, such as in biomass conversion and automotive exhaust remediation. The unique properties of zeolites are associated with the well-defined pores and channels of molecular dimensions. Because of the close structure-property relationship, numerous efforts have been made to synthesize zeolitic materials with new pore structures and compositions and subsequently explore their properties and applications. Therefore, a crucial part in the study of zeolitic materials is to determine the structure, more specifically, the atomic positions.

X-ray diffraction method has been applied for structural determination of crystalline materials for more than one century. However, challenges are still remaining on the structural analysis of nanocrystalline materials which are too small to be studied by single crystal X-ray diffraction. X-ray and neutron powder diffraction are the alternatives. Nevertheless, additional challenges rise due to their intrinsically limited one-dimensional information. The systematic and accidental peak overlapping is a common problem in powder diffraction when treating structures with large unit cell parameters, such as zeolites. Moreover, small crystal sizes and defects result in peak broadening, which in turn intensifies overlapping.

Electron crystallography has developed rapidly in recent years for structural determination of nano-sized crystals using transmission electron microscopy by taking the advantages of the short wavelength of electrons. Rotation electron diffraction (RED) is a semi-automatic technique developed for collection and processing of 3D electron diffraction data[1,2]. Nowadays, a complete continuous rotation electron diffraction (cRED) data can be acquired in 15-150 seconds using continuous goniometer tilt[3], and the electron dose can be limited to below 0.1 e/Å^2. The method has been used for analysis of complex structures, such as zeolites and MOFs, where the electron dose is crucial for limiting radiation damage. I will demonstrate the *ab initio* structure determination of an aluminophosphate molecular sieve, PST-5, which is among the most complicated zeolitic structures with 112 unique atoms. Notably, only by using *c*RED, we discovered a unique 3D-3D topotactic transformation, which takes advantage of weak bonding in PST-5, and transforms to PST-6[4]. By adopting the transformation, it may open a new way for synthesis of targeted zeolites, especially those which may not be feasible by conventional methods.

To further automate the data collection, we have developed SerialRED for automated data collection, processing, and structure solution[5]. The large number of particles makes it possible even for quantitative phase analysis, and for detection of minor phases that may not be detectable by X-ray diffraction. By applying SerialRED, a mixed phase of UiO-67/MIL-140C can be identified and well resolved automatically, where the peak overlapping makes it difficult by analysing PXRD data[6].

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Advanced Characterisation and Operando Spectroscopies|MOFs/Organic materials

FEZA21-OR-092

Following the formation of Zeolites and MOFs in-situ

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[1]6.5 Synthesis and Scattering of Nanostructured materials, Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, Germany, [2]I22: Small Angle Scattering & Diffraction, Diamond Light Source, Didcot, United Kingdom

Abstract Text: Porous materials are of a great interest due to their ability to interact with ions and molecules not only on their surface but throughout their bulk. Porous materials are conventionally used in applications; such as ion exchange, adsorption/separation and in catalysis, exploiting the huge internal surface area of highly ordered porous materials. [1, 2] The ability for these materials to succeed, in a particular field, is dependent greatly upon the uniformity of the shape and size of the pores within the material. However, despite how well we are able to understand the stability of 3-D frameworks in crystalline or polycrystalline zeolites and ZIFs, there still remains major limitations in fully understanding the synthetic mechanisms occurring prior to their formation. [3, 4] Though the syntheses of a wide variety of porous solids are already well established, their formation mechanisms continue to be of great interest to both academic and industrial communities, with the thought that with greater understanding of the formation of these solids can lead to their rational design. By obtaining a better knowledge of the underlying nucleation mechanisms, it can allow for increased predictability of new structures and in addition can reveal valuable information regarding the particle dimensions aiding in controlling particle morphology and size.

Small-angle and wide-angle X-ray scattering (SAXS/WAXS) are ideal techniques for determining morphological changes *in-situ*, where the shape, size and crystallinity can be followed at a high temporal resolution, and when these techniques are deployed alongside complimentary techniques, such as *ex-situ* microscopy, a great deal of information on the formation of materials can be obtained. The above-mentioned methodologies were utilised to study the formation of Silicalite-1 from multiple silica sources to obtain a detailed picture of the formation as a whole, including the formation of intermediate species (Image 1 show the *in-situ* SAXS data collected from the formation of Silicalite-1 from tetraethyl orthosilicate).

In-situ SAXS/WAXS studies were also utilized to observe the formation of ZIF-8 alongside *in-situ* X-ray absorption spectroscopy (XAS) experiments to probe both the morphological changes, as well as any changes occurring to the local structure during synthesis (Image 2 show the *in-situ* SAXS data collected from the formation of ZIF-8). These time-resolved *in-situ* studies have been utilised to follow changes in crystallinity and crystallite size, whilst also providing valuable information on the formation of intermediate species, the nucleation of crystalline ZIFs, and their subsequent growth.

Image 1:

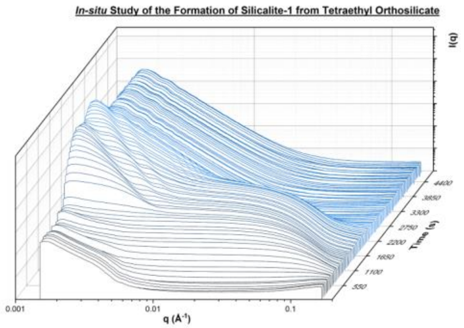
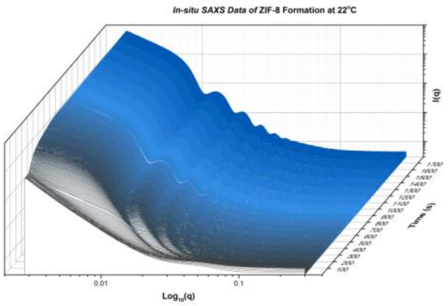


Image 2:



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Advanced Characterisation and Operando Spectroscopies|MOFs/Organic materials

FEZA21-OR-093

Unravelling the Guest Encapsulation in Metal-Organic Frameworks via Infrared Nanospectroscopy

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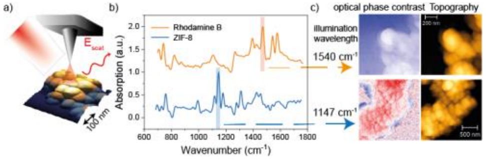
Abstract Text: Metal-organic frameworks (MOFs), constructed from the self-assembly of metal clusters and organic linkers, can provide exceptional porosity for molecular guest encapsulation useful for emergent applications in sensing, gas storage, drug delivery and optoelectronics. Central to the realisation of novel practical devices, however, is a fundamental understanding of the underlying host-guest interactions. Herein, we demonstrate, for the first time, the feasibility of scattering-type scanning near-field optical microscopy (s-SNOM) and nano-Fourier transform infrared (nanoFTIR) spectroscopy to reveal the vibrational characteristics of individual MOF-type nanocrystals. Taking a step further towards exploring the physical and chemical properties of MOFs, we present the first near-field spectroscopic evidence of the confinement of luminescent guest molecules in the host framework materials ZIF-8. To this date, it has been a major challenge to undoubtedly answer the question whether the guest molecule is successfully incorporated into the pore. By pinpointing the local molecular interactions at a 20 nm spot[1], we chemically study the confinement of the guest molecule by measuring topography and the infrared (IR) active modes of both constituent materials with nanoscale resolution, and further explain our findings with density functional theory calculations.

A close analysis of the nanocrystals leveraging nanoFTIR measurements and s-SNOM imaging elucidates the absence of any guest material on the crystal surface (fig. 1), while the photo-physical properties of the luminescent molecules are still observable. We conclude that the guest molecule is confined in the framework and thus, evince the guest@MOF principle[2-4]. Our findings not only confirm the encapsulation of guest molecules in the host framework, but further provide a template for future nanoscale-resolved physical and chemical analysis of metal-organic frameworks paving the way to controlling their unique properties — key to emergent applications.

Image 1: (unpublished data) *a) The illuminated AFM tip generates a nanofocus, the near-field interaction between the tip and the sample changes the scattered light, from which the local optical properties are derived. c) Near-field IR absorption spectra of rhodamine B (RhB) and ZIF-8. c) s-SNOM imaging proves that there are no traces of RhB on the surface of the ZIF-8 crystals.*

Image 1:



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Catalytic Properties

FEZA21-OR-094

Iron/Metal-Organic Framework (Fe-MOF)-based electrodes for direct nitrogen reduction reaction to ammonia in mild conditions

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Abstract Text: The nitrogen reduction reaction (NRR) to form directly ammonia (NH_3) under mild conditions is an emergent electrochemical process that has recently received a fast-growing attention [1]. Ammonia represents the basis for fertilizer industry with a 120 Mt/y world production, today dominated by the energy-intensive Haber–Bosch process that requires very high temperatures (400-600 °C) and pressures (20-40 MPa). Thus, a sustainable alternative process like the electrocatalytic NRR directly to ammonia in mild conditions is highly desirable [2]. However, one of the main issues of NRR is the low solubility of nitrogen in aqueous solutions, limiting the Faradaic Efficiency of the process and favouring the side-reaction of hydrogen production by proton reduction. The use of a gas absorbent element in the electrocatalyst formulation may improve nitrogen absorption enhancing its local concentration on the electrode active surface.

In this view, a series of advanced Iron/ Metal-Organic Framework (Fe-MOF)-based materials were prepared and assembled with a nanocarbon porous substrate to create a gas diffusion electrode for ammonia electrosynthesis. Specifically, Fe-based and Fe-alkali metal-based MOFs UiO-66-$(COOH)_2$ were synthesized by cation exchange reaction technique to replace the proton of carboxylic acid with an iron cation. UiO-66 is a zirconium (IV) based MOF with a highly stable $Zr_6O_4(OH)_4$ inorganic brick, where each Zr_6-Octahedra is bound to twelve 1,2,4-benzenedicarboxylic acid linkers. These new Fe-MOFs UiO-66-$(COOH)_2$ are very stable both in water and air and do not contain nitrogen atoms in their structure, thus eliminating the problem of false positive in ammonia detection (potentially coming from the MOF structure and not from molecular nitrogen), which is a current element of discussion in NRR community.

The as-prepared Fe-MOF materials were fully characterized by Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), N_2 adsorption/desorption isotherm for BET surface area analysis. Then, the Fe-MOF electrodes were tested as electrocathodes for the process of ammonia electro-synthesis starting from H_2O and N_2 in an advanced gas–liquid–solid three-phase reactor [3], working at room temperature and atmospheric pressure.

Results evidenced that 80% cation exchange Fe@UiO-66-$(COOH)_2$ (with an effective Fe content of around 8 wt.%) was the best electrocatalyst among the tested Fe-based MOF synthesized materials, providing an ammonia yield of 1.2 $\mu g \cdot h^{-1} \cdot mgcat^{-1}$. The effect of applied voltage was also explored, indicating an optimal potential of -0.5 V vs. RHE to maximize activity in NRR and limiting the side hydrogen evolution reaction. Moreover, as currently used in industrial catalysts for Haber-Bosh process, the introduction of potassium in the electrocatalysts was also investigated, in order to facilitate charge transfer from K^- ions to the iron-based catalyst surface, balancing the dissociative chemisorption between H_2 and N_2, and suppressing side reactions, thus improving both activity and stability. A linear trend was observed between ammonia production rate and BET surface area, suggesting a direct relationship between these two aspects. Moreover, a higher iron content exhibited better catalytic activity. The results of this work are very promising, and further experimentation is now under progress to overcome limitations related to MOF materials themselves, majorly due to their low conductivity.

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Catalytic Properties|MOFs/Organic materials

FEZA21-OR-095

Dispersible Microporous Polymers as Supports for Carbonylation Catalysts

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Abstract Text: Microporous organic polymers (MOPs) are a class of materials that are both chemically and thermally stable, easily functionalised, cheap to produce and readily scalable. These features make them attractive candidates as solid supports for a range of applications, including catalysis. Recently, a new class of porous materials have been synthesised via the union of hypercrosslinking and reversible addition-fragmentation chain transfer-mediated polymerisation-induced self-assembly (RAFT-mediated PISA).[1] This allows for the synthesis of dispersible microporous nanoparticles with a core-shell structure, which combine the advantages of insoluble microporous materials with dispersibility in a range of solvents due to their long hydrophilic coronae. This makes them ideal supports for catalysts given that they mix well in solution but are much more easily retrieved than soluble catalysts.

Methanol carbonylation is an important industrial process for the production of acetic acid, a major feedstock chemical for which demand exceeds 18 million tonnes per annum. The Monsanto and Cativa™ processes are the preeminent methods in the bulk manufacture of acetic acid. However, as homogeneous systems, they suffer from the need to recycle the dissolved catalyst. Previously, efforts have been made to heterogenise these catalysts on a range of solid supports, including polymers.[2]

Dispersible microporous polymer nanoparticles containing 4-vinylpyridine and 1,4-divinylbenzene (1:1) monomers and a polyethylene glycol (PEG) based macro-chain transfer agent (CTA) were synthesised (Image 1). The PEG-based macro-CTA both mediated the copolymerisation and facilitated the dispersibility of the resulting nanoparticles in a wide range of common organic solvents. The bifunctional nature of 1,4-divinylbenzene led to a hypercrosslinked microporous core, with a BET surface area exceeding 350 $m^2\ g^{-1}$.

Post-synthetic modification via methylation of the pyridine nitrogen sites gave a cationic support with iodide counter-ions in its pores (Image 2). This was then used to electrostatically immobilise the active catalyst for the Monsanto process, *cis*-$[Rh(CO)_2I_2]^-$ (Image 2).

Volumetric N_2 gas sorption studies suggested that the catalyst occupied the micropores in the core of the nanoparticles. By virtue of the long-term stability of suspensions of these materials, the reaction of the supported catalyst with iodomethane (the rate-limiting step of the Monsanto catalytic cycle) could be monitored *in situ* using IR spectroscopy. This suggested a tenfold rate increase for the supported catalyst compared with the analogous homogeneous reaction. The supported catalyst was found to be active for the carbonylation of methanol, with a slightly lower turnover frequency than the homogeneous analogue.

To summarise, microporous polymer nanoparticles have been synthesised that are capable of dispersion in a wide range of common organic solvents. They have been used to heterogenise the active catalyst in the Monsanto process, *cis*-$[Rh(CO)_2I_2]^-$, in its micropores. These materials have been extensively characterised, and the key catalytic steps observed *in situ*. The supported catalyst was found to be active for the carbonylation of methanol, thus marking a major improvement on the existing homogeneous process.

Image 1:

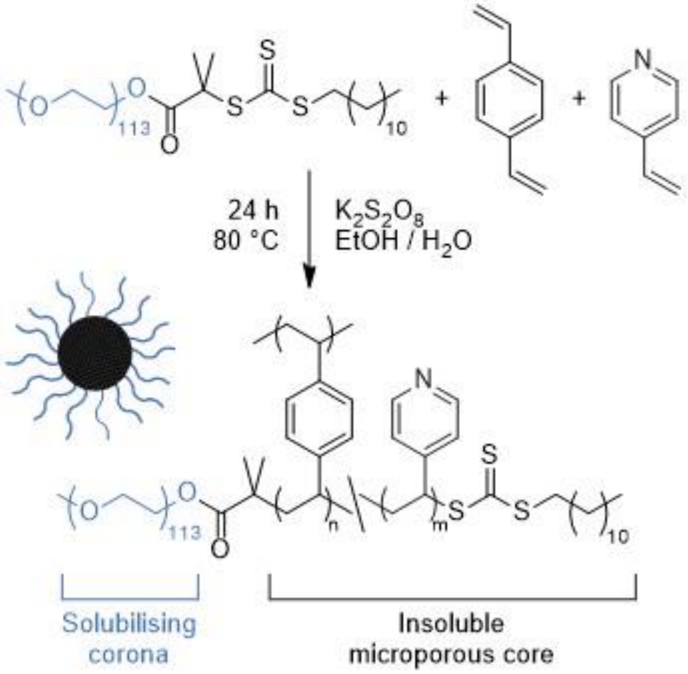
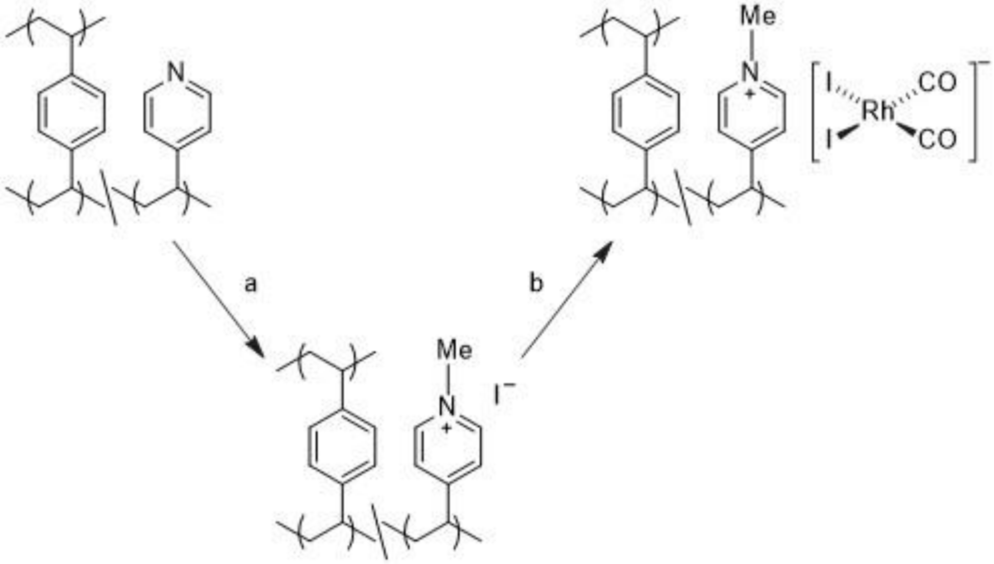


Image 2:



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Catalytic Properties|MOFs/Organic materials

FEZA21-OR-097

MOF-derived zeolite hybrid catalysts for CO2 to olefins and fine chemical catalysis

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Abstract Text: In this contribution we propose an alternative catalytic system based on MOF derivatives and silicoaluminates for the selective CO_2 conversion into light olefins and to selectively modify important bio-active scaffolds in a clean and efficient manner, using the lowest metal loadings reported in literature. The new general heterogeneous catalytic methodology presented here is based on the solvent-free grounding and co-calcination of catalytic amounts of MOFs with aluminosilicates. This is an interesting alternative to the use of co-precipitated bulk metal oxides due to the fact that the metal oxide sites are atomically dispersed in a metal organic crystalline framework and thus, it should produce less agglomerated/ smaller nanoparticles after thermal decomposition of the linker in the close vicinity of the zeolite.

On the one hand, we propose the use of aluminosilicate zeolites with the same CHA topology as zeotype SAPO-34, but with different acid strengths, and we compare their catalytic performances for the direct transformation of CO_2 into light olefins. Our attention is focussed on the use of In-Zr mixed metal organic frameworks (MOFs) as precursors of redox active and robust supported $(In\text{-}Zr)O_x$ nanoparticles uniformly distributed along with the mentioned aluminosilicates (i.e. SSZ-13), after its thermal decomposition (Image 1). Both the well-dispersed and low loaded MOF derived In-Zr oxide and the strong acidity of chabazite-type zeolite acts cooperatively in the activation of CO_2 and C-C couplings resulting into 334 mmol of light olefins per gram of In and hour at 400ºC, among the highest reported value in literature.

On the other hand, this solid-state synthesis allows to generate MOF (HKUST-1 or MOF-5) derived non-precious metal oxide nanoparticles (CuO or ZnO) over aluminosilicates (USY or MCM-41), as catalysts in C-C (alkynylation, alkylation, aldol condensation, hetero-Diels-Alder) and C-N (amination) bond formations to make propargylamine, (spiro)(ox)indole and quinoline derivatives (image 2), with the highest TOFs ever reported for simple H^+/Zn/CuO active sites. The higher availability of this metal oxide sites when they are dispersed within the porous matrix with respect to bulk metal-oxide or metal-organic framework, results in a better activity (TOFs up to two orders of magnitude higher) and reusability (by simple calcination), compared to the pure MOF.

Image 1:

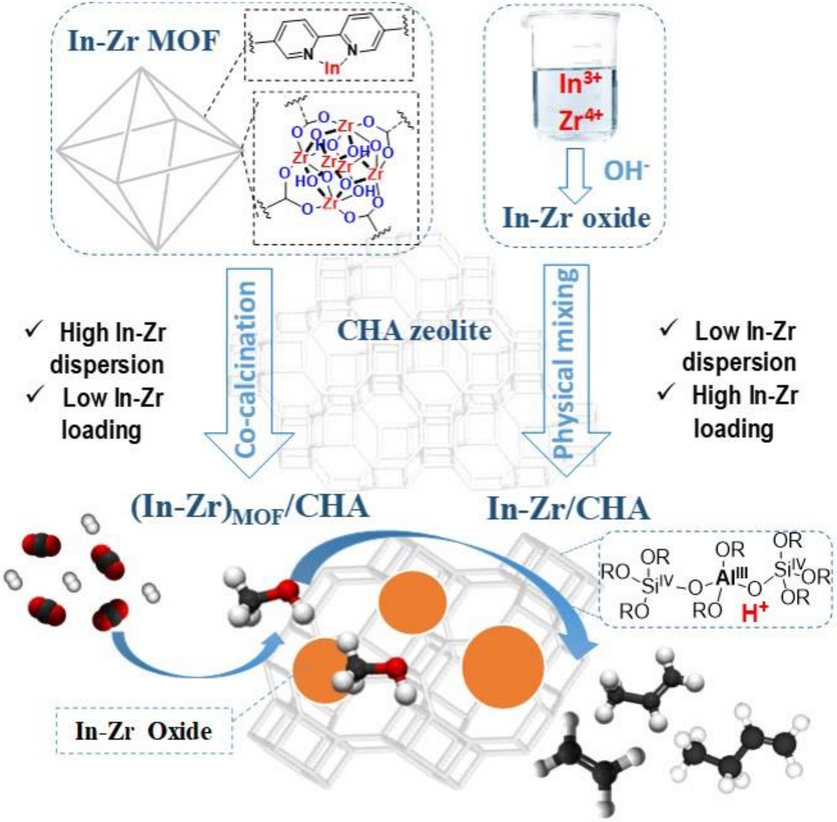
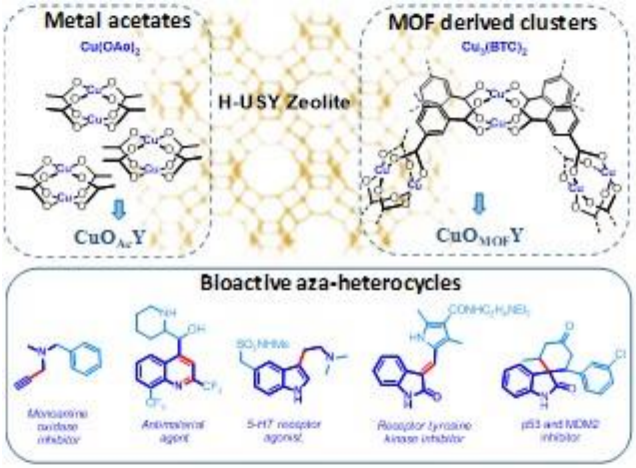


Image 2:



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Catalytic Properties|MOFs/Organic materials

FEZA21-OR-098

Sulfide Organic Polymers (SOPs) as efficient heterogeneous catalysts for esterification, thioesterification and amidation reactions

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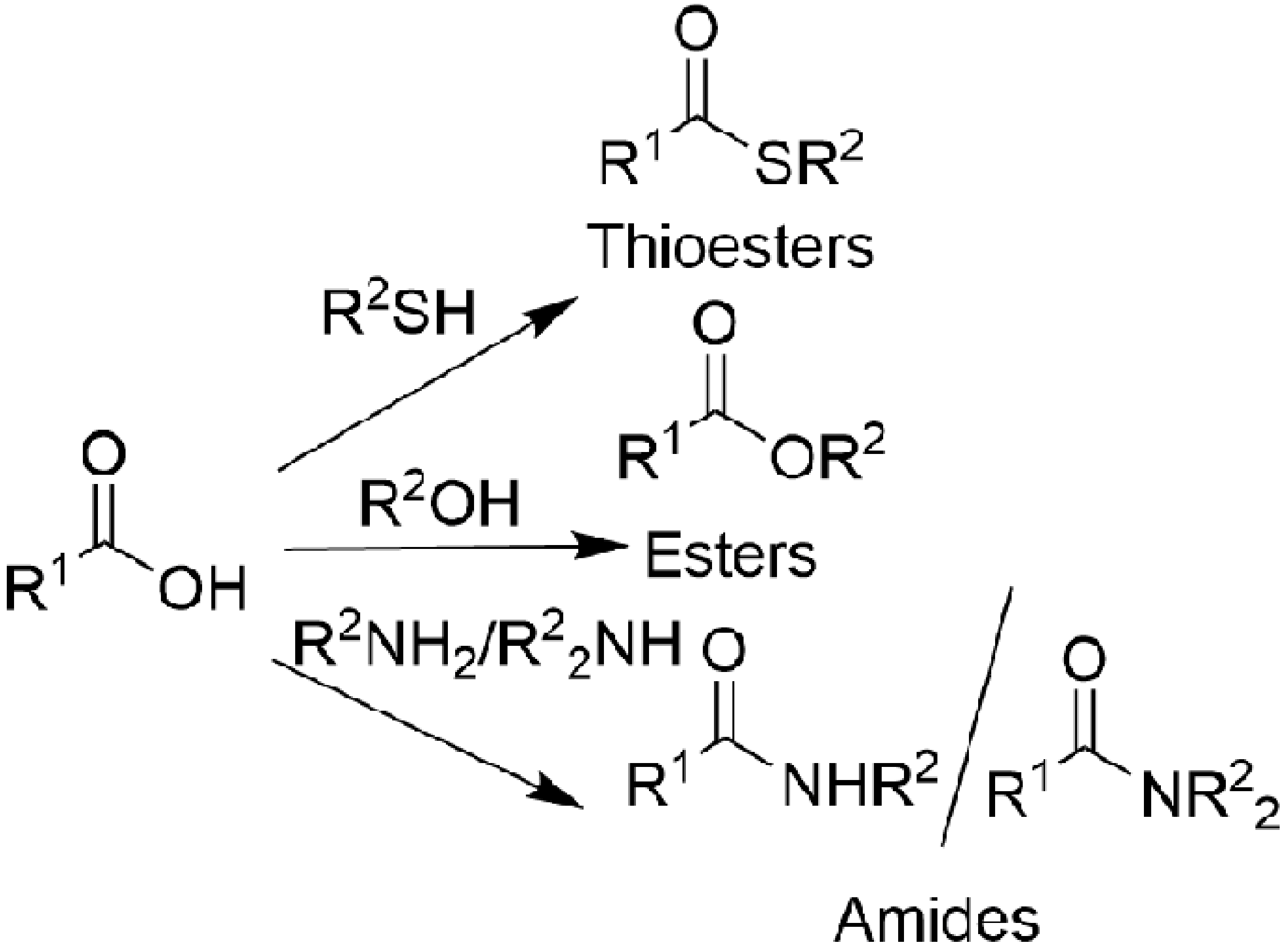
Abstract Text: Covalent organic polymers (COPs) are a type of supramolecular compounds, formed by self-assembly of organic building units through covalent bonds [1-3]. They have recently emerged as a molecular platform for designing promising organic materials. Thus, interesting novel sulphur organic polymers with improved properties are being actively sought for further applications. In this work, we report on the synthesis of two organosulfide based covalent organic polymers named SOP-1 obtained via click process through SN2 reaction and SOP-2 via thiol-yne reaction. Solid state 13C NMR and FT-IR spectroscopic data confirm the synthesis and integrity of SOP-1 and SOP-2. Herein, we will show that SOP-1 and SOP-2 are active and reusable heterogeneous catalysts for esterification, thioesterification and amidation reactions, resulting in high conversions of the expected esters, thioesters and amides, respectively. These reactions are industrial relevant ways towards the preparation of numerous high added value products [4-8]. The organosulfide compounds SOP-1 and SOP-2 are able to activate the carboxylic acid through nucleophile catalysis mechanism. Thereby, SOP-1 and SOP-2 are interesting alternative to typical Fischer esterification acid catalysts, while avoiding the use of stoichiometric amounts of sacrificial coupling agents, such as dicyclohexylcarbodiimide (DCC) or 2,4,6-trichlorobenzoyl chloride.

Image 1:



Catalytic reactions performed with SOPs

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Gas Adsorption, Separation and Storage

FEZA21-OR-099

Ammonia capture via an unconventional reversible guest-induced metal-linker bond dynamics in a highly stable Metal-Organic Framework

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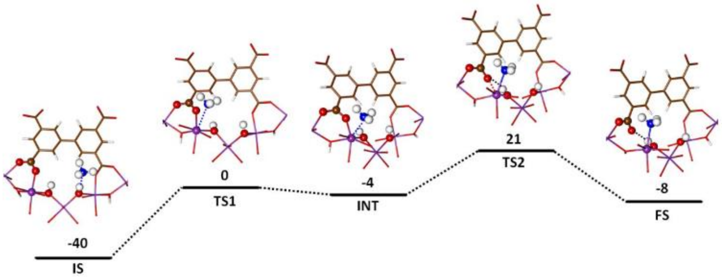
Abstract Text: Ammonia (NH_3) capture by an adsorbent is highly challenging due to its high toxicity and chemical reactivity. The family of Metal-organic frameworks (MOFs) has attracted a significant attention owing to the large NH_3 uptake and high chemical stability demonstrated by some of these materials. To date, a full understanding of the NH_3 adsorption mechanism in this class of porous solids is still far to be achieved. Indeed, this knowledge is of utmost importance to further design NH_3 MOF adsorbents with refined performances.

Herein, we report an unprecedented reversible guest-induced metal-linker bond rearrangement in MOFs upon ammonia adsorption as revealed by quantum-calculations and supported by DRIFT experiments. As a show-case, the prototypical MOF-type MFM-300(Sc) was demonstrated to undergo a substantial Sc-carboxylate bond dynamics upon ammonia adsorption to enable a strong metal-guest binding adsorption mode, a key feature to ensure a highly efficient capture of this toxic molecule.

Periodic Density Functional Theory (DFT) calculations were first performed to probe diverse NH_3 adsorption modes in MFM-300(Sc). A possible reaction path involving a metal-carboxylate bond dynamics upon NH_3 adsorption was identified with the climbing image nudged elastic band (CI-NEB) method. As shown in Fig. 1, the reaction proceeds via the formation of an intermediate state (INT) where the guest molecule relocates from the μ-OH site to a neighbor Sc atom and induces an elongation of one Sc-O bond. This local structure reorganization occurring throughout a first transition state (TS1) is reminiscent of the thermal-driven loose state for a metalcarboxylate bond very recently demonstrated for some typical MOFs.[1] It ends up with the complete breaking of the Sc-O bond and the formation of a hydrogen-bond type interaction between the dangling O-atom with the neighbor μ-OH group in the final state (FS) via a second transition state (TS2). *Ab* initio molecular dynamics (AIMD) was further employed to show the stability of such alternative NH_3 adsorption configuration. Interestingly, further AIMD calculations evidenced that once NH_3 is removed from such configuration, the MOF framework is self-healed and its initial crystal structure is regenerated. Therefore, this NH_3-triggered dynamic metal-linker bonding is demonstrated to be fully reversible which accounts for the experimentally observed adsorption/desorption behavior of MFM-300(Sc). These theoretical findings were supported by further DRIFT experiments. Such unconventional mechanism in MOFs can open new avenues to design novel materials for an efficient capture of highly corrosive molecules.

Image 1:



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Gas Adsorption, Separation and Storage

FEZA21-OR-100

Tuning the gate opening in zeolitic imidazolate frameworks by metal substitution

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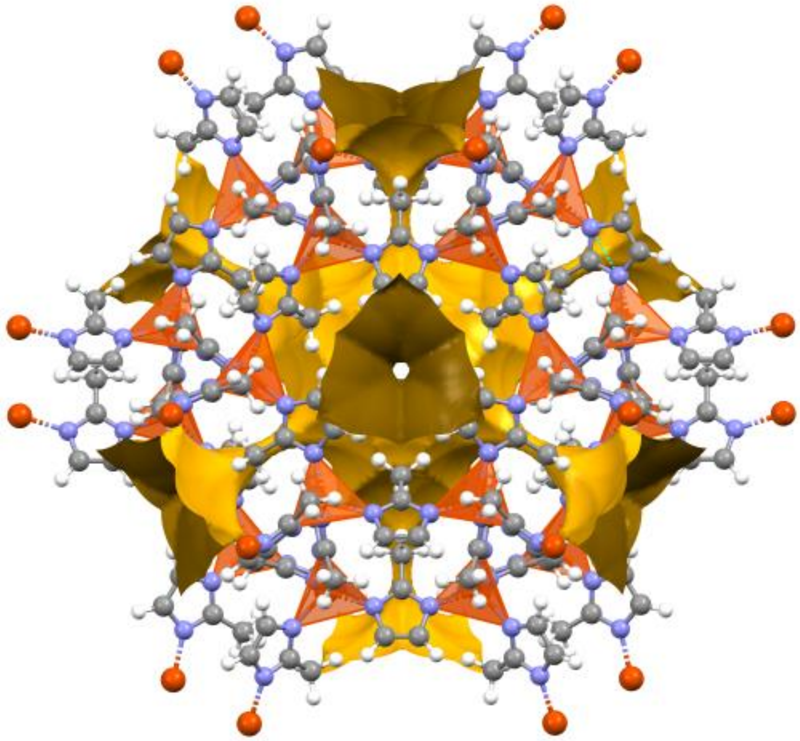
Abstract Text: The pressure-induced rotation of the imidazolate in Zeolitic Imidazolate Frameworks (ZIFs) is accompanied by an increase of ZIF pore openings, affecting ZIFs performance in separation processes. This phenomenon is known as the gate opening or the swing effect.[1,2] We show by using periodic Kohn-Sham density functional calculations that metal substitution (Mg, Fe, and Zn) is a very effective way to tune the flexibility of ZIF-8 materials. For both the magnesium- and the iron-based system the gate opening phenomenon requires half and a fourth of the energy than for the zinc material, respectively.[3] The metal determines also the most stable phase of the material. Because of the importance of ZIF-8 among porous materials and because the gate opening is its most studied property, our results strongly call for future high-pressure diffraction studies aimed at the experimental verification of the present findings.

Image 1:



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Gas Adsorption, Separation and Storage|MOFs/Organic materials

FEZA21-OR-101

Nanoporouspolymer-based composites for enhanced hydrogen storage

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Abstract Text: The exploration and evaluation of new composites possessing both processability and enhanced hydrogen storage capacity are of significant interest for onboard hydrogen storage systems and fuel cell-based electric vehicle development. Here we demonstrate the fabrication of nanoporous composite membranes with sufficient mechanical properties for enhanced hydrogen storage that are based on a polymer of intrinsic microporosity (PIM-1) matrix containing nano-sized fillers: activated carbon (AX21) or metal organic framework (MIL- 101). The composite films were characterised by surface area and porosity analysis, hydrogen adsorption measurements, mechanical testing and gas adsorption modeling. The PIM-1/AX21 composite with 60 wt. % AX21 provides enhanced hydrogen adsorption kinetics and a total hydrogen storage capacity of up to 9.35 wt. % at 77 K; this is superior to the US Department of Energy hydrogen storage target. Tensile testing indicates that the ultimate stress and strain of PIM-1/AX21 are higher than those of the MIL-101 or PAF-1 containing composites, and are sufficient for use in hydrogen storage tanks. The data presented provides new insights into both the design and characterisation methods of polymer-based composite membranes. Our nanoporous polymer-based composites offer advantages over powders in terms of safety, handling and practical manufacturing, with potential for hydrogen storage applications either as means of increasing storage or decreasing operating pressures in high-pressure hydrogen storage tanks.

Image 1:

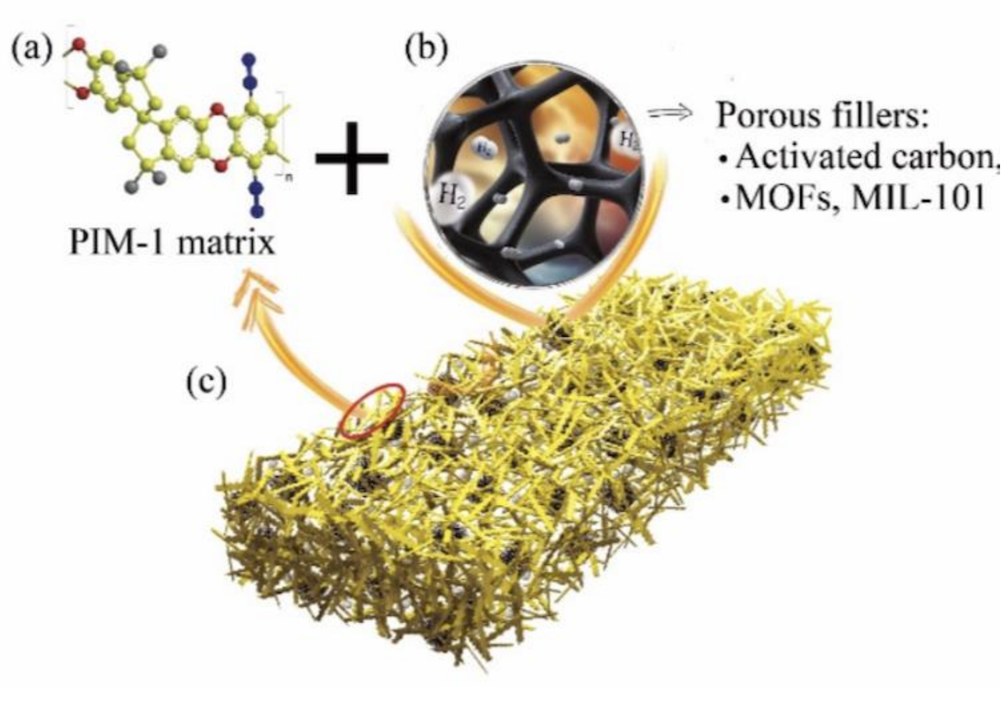
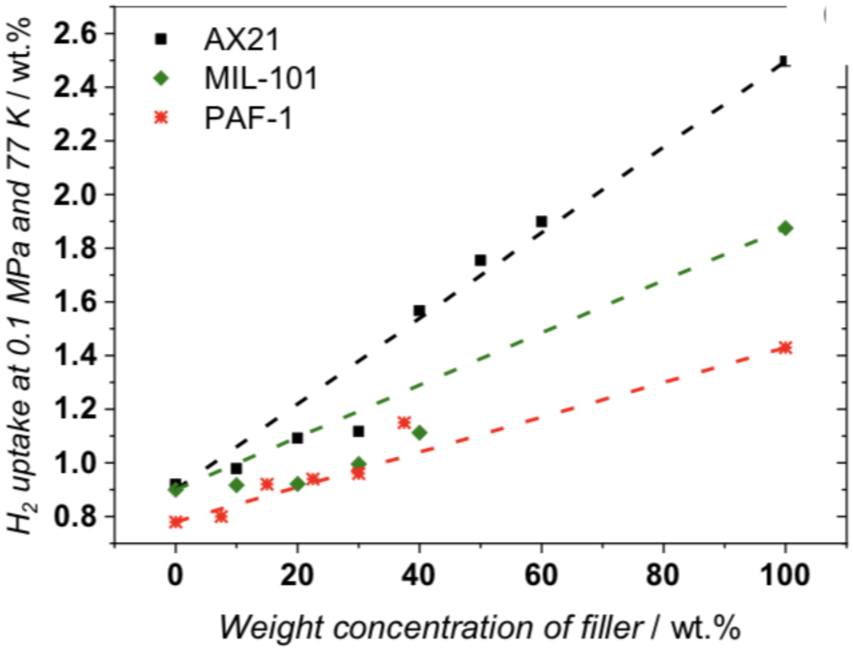


Image 2:


■ AX21
◆ MIL-101
✱ PAF-1
H_2 uptake at 0.1 MPa and 77 K / wt.%
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0
20
40
60
80
100
Weight concentration of filler / wt.%

Gas Adsorption, Separation and Storage|MOFs/Organic materials

FEZA21-OR-102

Ammonia Capture in a Robust Aluminium Metal-Organic Framework Decorated with Free Carboxylic Acid Moieties

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Abstract Text: Ammonia is recognised as one of the five most damaging pollutants and can combine with urban NO_x to contribute to smog formation in the atmosphere.[1] In addition to being detrimental to human health, ammonium deposition also causes significant long-term harm to sensitive habitats which can reduce biodiversity.[2] However, contrary to its hazardous properties, ammonia is also regarded as one of the best media for the storage and distribution of hydrogen for the hydrogen economy.[3] To exploit this potential, researchers have been challenged with finding safe and high-capacity storage media, as well as effective capture and removal systems for any leached ammonia. Porous materials, including zeolites, MOFs and activated carbons, have shown promise,[4–6] but are usually limited in their scope due to the corrosive nature of ammonia.

Herein we report the synthesis of a new aluminium MOF, MFM-303, which is found to not only be stable to a wide range of pH, solvent environments and ammonia but can accommodate high ammonia packing density. The structure of MFM-303 contains unbound carboxylic acid moieties which is relatively uncommon in MOFs due to the strong binding affinity of oxygen to metal centres. MFM-303 also possesses μ_2-OH groups pointing along the pore walls, resulting in a narrow pore aperture.

The adsorption of ammonia into MFM-303 was found to be rapid at low pressures, with ~60% of the total uptake capacity (9.9 mmol g^{-1} at 273 K, Image 1) achieved at 2 mbar. Thus, the MOF was tested for dynamic ammonia capture at low concentrations via gas breakthrough experiments. These experiments showed that NH_3 was retained for extended periods under both dry and humid conditions and that 69 % of the maximum capacity was attained under dynamic dry flow due to the fast adsorption kinetics.

To understand these promising adsorption properties, high resolution *in-situ* PXRD experiments were undertaken. From these, the ammonia adsorption sites within the framework were located (Image 2), highlighting the free –COOH and the μ_2-OH groups as the main binding domains. Inelastic neutron spectroscopy data coupled with DFT modelling corroborated these findings from a dynamic perspective and the role of the μ_2-OH group, in particular, was highlighted.

From this work, MFM-303 gives direct evidence that free carboxylic acid groups can provide strong adsorption sites for binding small guest molecules. We have thus demonstrated there is much potential for MOFs containing free carboxylic acid groups for the dynamic capture or storage of ammonia.

Image 1:

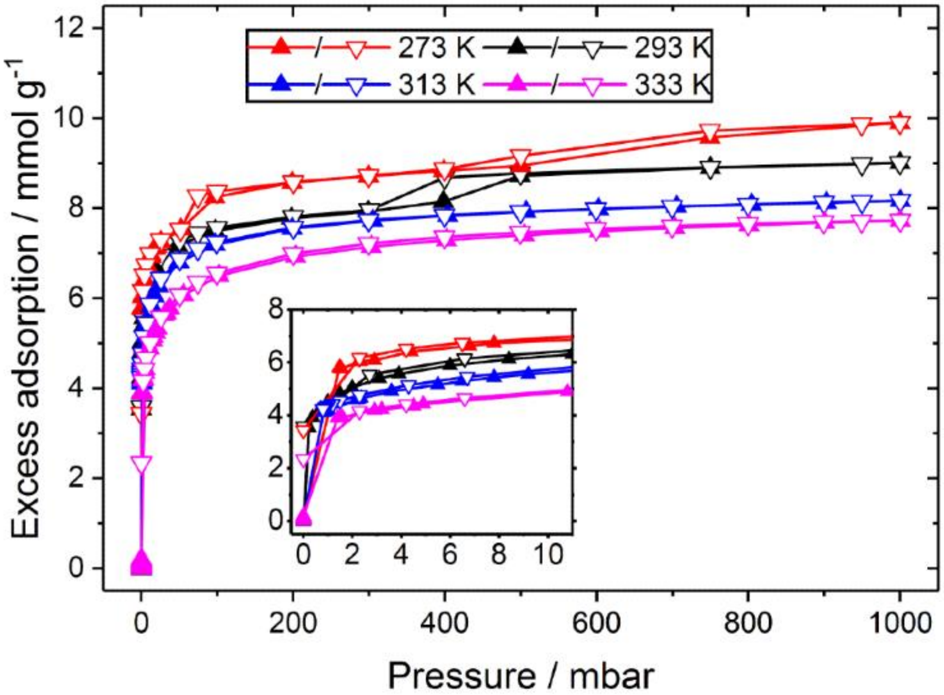
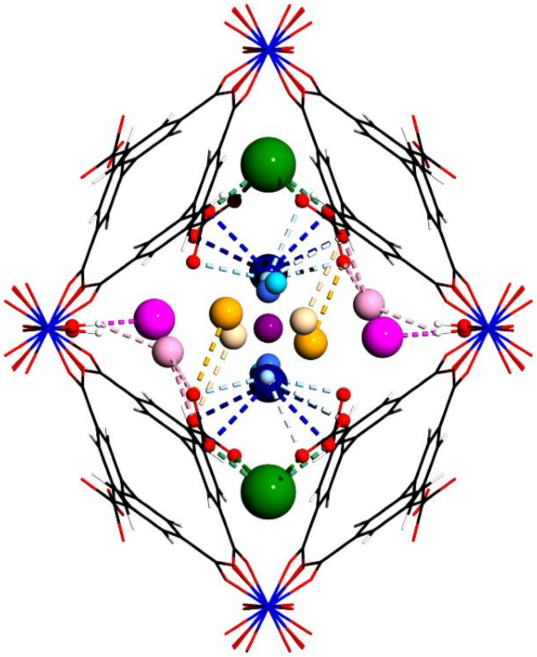


Image 2:



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Gas Adsorption, Separation and Storage|MOFs/Organic materials

FEZA21-OR-103

Modeling of Gas Transport through Polymer/MOF Interfaces: A Microsecond-Scale Concentration Gradient-Driven Molecular Dynamics Study

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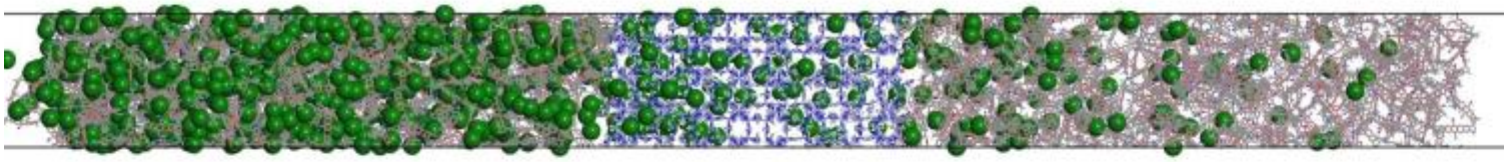
Abstract Text: Despite efforts to understand the molecular basis of polymer/MOF compatibility, no correlation has yet been found between compatibility and the performance of these composites for different applications. Even though the presence of microscopic sized voids at the interface has been clearly related to the formation of brittle membranes (i.e., nonoptimal mechanical properties), the speculation that the presence of these voids might lead to a reduction in selectivity has never been confirmed. Conversely, the absence of these voids is a signature of good polymer/MOF compatibility, but this is not necessarily related to the good performance of the corresponding membrane for a particular application.

To address this still open question, we report microsecond-long concentration gradient-driven molecular dynamics (CGD-MD) simulations of H2 and CH4 transport in PIM-1 and ZIF-8 membranes as well as their permselectivity in the composite PIM-1/ZIF-8 membrane, with a specific focus on gas transport properties through the interfaces as well as along the individual components of the miced-matrix membrane. The CGD-MD method allowed us to map the density and mean residence time profiles of the H2 and CH4 gases along the membranes while these two gases diffuse under a concentration gradient. Furthermore, we directly computed the flux of the permeating gases through the membranes from the CGD-MD simulations and evidenced the effect of the interfaces on the H2/CH4 permselectivity in the composite PIM-1/ZIF-8 membrane. We found that the presence of nonselective void spaces between PIM-1 and ZIF-8 in the composite PIM-1/ZIF-8 membrane induces a decrease of the H2/CH4 permselectivity by about 20% compared to the ideal permselectivity estimated by the application of macroscopic model on the data obtained individually for ZIF-8 and PIM-1. The CGD-MD simulations carried out with an accurate description of the polymer/MOF interfaces allow the determination of the magnitude of such a deviation, thus paving the way for a more critical use of macroscopic models to predict the performances of MMMs. This work provides a first unambiguous proof that interfaces play a crucial role in the gas transport mechanism in polymer/MOF composites. This makes questionable the extensive use of macroscopic models to predict the performances of MMMs, since these models do not take into account either defects at the interface or interactions between guest molecules in gas mixtures, factors that have a big impact in the performance of the MMM.

Image 1:



References: Chem. Mater. 2020, DOI: 10.1021/acs.chemmater.9b04907

Gas Adsorption, Separation and Storage|MOFs/Organic materials

FEZA21-OR-104

Probing Zeolitic Imidazolate Frameworks (ZIFs) for heat storage applications

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Abstract Text: The ability to supply sufficient energy and heat in an environmentally friendly manner to the rapidly growing population is of great importance. One method that addresses this issue and uses renewable energy is Thermal Energy Storage (TES), which uses the reversible chemical reactions and/or sorption processes of gases in solids or liquids. One major benefit of using this method is that it only shows an insignificant amount of heat loss while reaching a considerably higher energy storage density. Sorption thermal energy storage can be examined using traditional adsorbents (*e.g.* zeolites) or innovative adsorbents (*e.g.* metal-organic frameworks). One of the subgroups of MOFs is Zeolitic Imidazolate Frameworks (ZIFs), which are comprised of transition metal ions (Zn, Co, etc.) and imidazolate linkers. ZIFs are structured similarly to zeolites with where the metal ion replacing the Si/Al and the imidazolate linker replacing the O atoms. The use of ethanol as a sorbate has seldom been explored but may prove to be beneficial for applications at lower temperatures [1, 2].

This presentation will discuss the synthesis, characterisation and ethanol sorption studies of a number of ZIFs (ZIF-8, ZIF-62, ZIF-71 and ZIF-90), which were performed to better understand the effect of topology and type of framework-sorbate interactions on the sorption performance and to evaluate their heat storage potential. The materials were synthesised using optimised methods based on literature data. The activation of the ZIFs was achieved using various methods, for example *via* calcination at 300°C (ZIF-62) and soaking in methanol followed by drying in vacuum oven at 150°C (ZIF-90). Structural properties were checked by XRD, TG, SEM/EDX, and nitrogen physisorption and revealed phase pure products. Ethanol sorption analyses were performed by an IGA-100 gravimetric analyser (Hiden Isochema Ltd.). The isotherms were collected at two different temperatures 25°C and 30°C in the relative pressure range from 0 – 0.9 in order to elucidate adsorption enthalpies. The results showed that the capacity up to 35 wt. % ethanol could be reached and that mechanism of sorption of ethanol in selected ZIFs were dominated by diffusion limitations of the molecules through the pores.

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Gas Adsorption, Separation and Storage|MOFs/Organic materials

FEZA21-OR-105

Computational Characterisation and Screening of Zr-Oxide Metal Organic Frameworks for CO2 Capture

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Abstract Text: Zr-oxide MOFs are known for their stability and have been gaining much attention for gas adsorption and separation applications. Here, we report structure search methods within the Cambridge Structural Database (CSD) through a number of “look-for-Zr-oxide-MOFs” criteria to identify and create a curated database of ca. 100 materials synthesised to date, bringing a unique record for all researchers working in this area. For all identified structures, we manually corrected the position of bridging hydroxyl groups, performed surface area characterisation, and calculated the partial atomic charges for each MOF using systematic density functional theory (DFT) methods. We then identified top-performing MOFs for post-combustion CO_2 capture via high-throughput grand Canonical Monte Carlo (GCMC) simulations (Figure 1 and 2). Through experimental verification of CO_2 adsorption in Zr-oxide MOFs, we revealed the importance of choosing the appropriate DFT functionals and basis sets to calculate electrostatic interactions at the Henry’s regime for CO_2 adsorption. The screening process also identified the top-performing Zr-oxide MOFs for post-combustion CO_2 capture with the capacity of up to 5.5 mol/kg at 298 K and 0.15 bar.

Image 1:

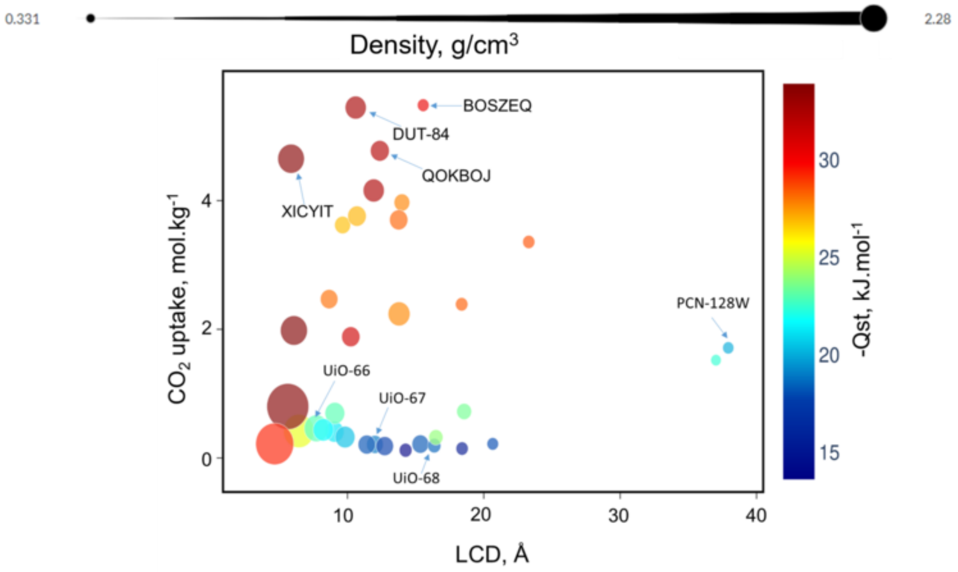
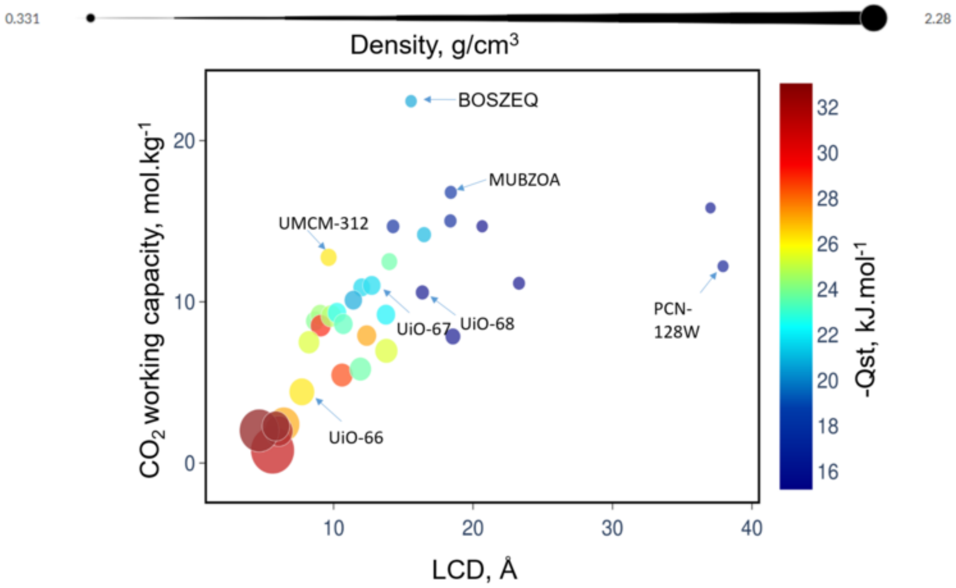


Image 2:


0.331
2.28
Density, g/cm3
BOSZEQ
MUBZOA
UMCM-312
UiO-67
UiO-68
PCN-
128W
UiO-66
CO2 working capacity, mol.kg-1
0
10
20
10
20
30
40
LCD, Å
32
30
28
26
24
22
20
18
16
-Qst, kJ.mol-1

Gas Adsorption, Separation and Storage|MOFs/Organic materials
FEZA21-OR-106

Energy efficient ultrahigh flux separation of oily pollutants from water with superhydrophilic nanoscale metal-organic framework architectures

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[2]Computer-Chemistry-Center, Department of Chemistry and Pharmacy, Friedrich-Alexander University Erlangen–Nürnberg (FAU) , Erlangen , Germany

Abstract Text: The growing demand for clean water is amongst the prominent issues of our time. Here, we introduce the synthesis of pillar-like metal-organic framework (MOF) crystallites, the metal-catecholate Co-CAT-1 (Co-hexahydroxytriphenylene), onto gold-coated woven stainless steel large aperture meshes (50 µm aperture). These nanostructured mesh surfaces feature superhydrophilic and underwater superoleophobic wetting properties, allowing for energy efficient, gravity-driven and highly efficient oil-water separation, featuring water flux of up to one million L m^{-2} h^{-1}. Water physisorption experiments reveal the hydrophilic nature of Co-CAT-1 with a total water vapor uptake at room temperature of 470 cm^3 g^{-1}. Furthermore, semiempirical molecular orbital calculations shed light on water affinity of the inner and outer pore surfaces. The MOF-based membranes enable high separation efficiencies for a number of tested liquids including the notorious water pollutant, crude oil. The crude oil effluent affords chemical oxygen demand (COD) concentrations below 25 mg L^{-1}, indicating the high quality of the water which is suitable for disposal as waste water. Our results demonstrate the great impact of suitable nanoscale surface architectures as a means for encoding on-surface extreme wetting properties, yielding energy-efficient water-selective large-aperture membranes.(1)

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MOF application

FEZA21-OR-108

Computational guided discovery of novel MOFs for Water-Adsorption Driven Heat allocation

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Abstract Text: There is nowadays a growing interest to search for novel porous solids able to achieve high uptakes of water at low relative pressure, which is one of the major requirements for adsorption-driven heat pumps and chillers. Such a process based on reversible adsorption/desorption of a fluid rather than conventional vapor compression is a promising alternative to exploit low-grade waste thermal energy for heat and cold allocation. MOFs represent a great source of inspiration for water sorption applications because of their tunable chemical and topological features associated with a larger variability of pore size. The MOF CAU-10 (CAU stands for Christian-Albrechts-University) is especially of interest for its very good hydrothermal stability, low cost, and low toxicity. A computational approach has been further devised to design isoreticular architectures by replacing the isophthalate linker by a series of linkers with the objective to design refined MOFs for the target application. Following this concept two new Al-MOF incorporating furandicarboxylate and thiophene dicarboxylate linkers were discovered with water adsorption performances in excellent agreement with the predicted ones. A third even more attractive MOF has been very recently devised and will be also discussed in the presentation.

MOF application

FEZA21-OR-109

Development of a new class of adaptable free-standing hydroxide-ion exchange membranes based on metal-organic frameworks for alkaline fuel cells

P. A. Szilagyi*

Abstract Text: *P. Kasongo-Ntumba[1], S. Herou[1,2], A. Prakash[1], Sz. Doszczeczko[1], M. Jum'Ah Yahya[1], A. Bushby[1], A. B. Jorge Sobrido[1], M.-M. Titirici[1,2], and P. Á. Szilágyi[1*]*

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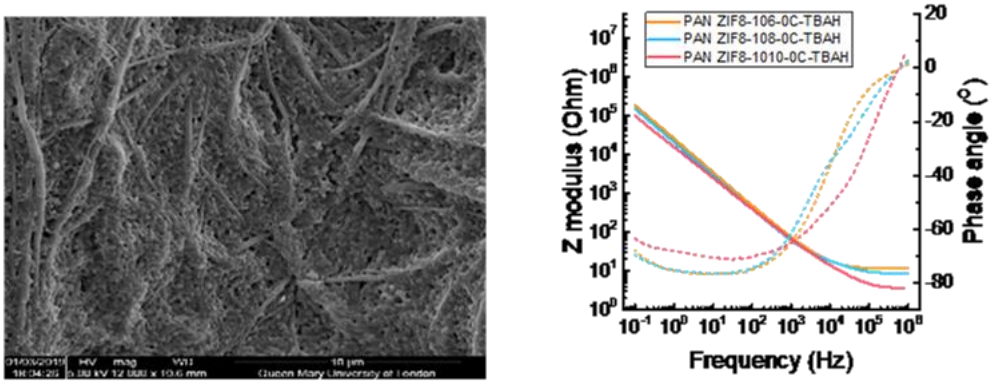
The increase of global demand of energy, the decrease of fossil fuels, and increasing atmospheric greenhouse gas levels prompted research into green alternative energy carriers and vectors. Hydrogen has been identified as a promising energy vector, whose oxidation in a fuel cell only results in the formation of water, while it directly converts the chemical energy to electricity. For instance, proton-exchange membrane fuel cells (PEMFC) offer the possibility to operate at low temperature, with reasonable size and without CO_2 emission. However, their drawbacks include high price of the platinum catalyst it requires. In this context, the use of alkaline fuel cells (AFC) could seem ideal, since the electro-catalysts are relatively inexpensive in comparison with PEMFC.[1]

In an AFC, the electrodes are separated by a membrane which is permeable for hydroxide ions. However, currently no membranes meet the stringent requirements that range from stability, ion conductivity to membrane costs, which warrants further research in the area. Metal-organic frameworks (MOFs) have emerged as a class of crystalline porous materials displaying advantageous properties particularly for tuneable host-guest interactions and improving processability, which makes them desirable hydroxide-ion exchange membrane materials.[2]

In this presentation I will discuss the development and optimisation of robust, adaptable, and scalable free-standing hydroxide ion (OH^-) conducting membranes, based on the metal-organic framework ZIF-8. The membranes were post-synthetically modified by grafting a hydroxide-containing ionic liquid on the pores [3], a procedure that enables the retention of both crystallinity and membrane flexibility. The obtained membranes have ambient-temperature ion conductivities of *ca.* 20 mS cm^{-1}, significantly improved through nano-structuration, surpassing that of Nafion® (*ca.* 5 mS cm^{-1}), approaching the scale of current record-holder anion conducting polymers (132 mS cm^{-1} at 80 °C) at ambient temperature.

Left Scanning electron micrograph of a self-supporting MOF-based membrane for alkaline fuel cells; R**ight** Representative Bode plots of selected MOF/IL membranes

Image 1:



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New Synthetic Methods and Post-Synthetic Modification|MOFs/Organic materials

FEZA21-OR-111

Mechanochemical Synthesis of Mixed Metal, Mixed Linker Glass-Forming Metal–Organic Frameworks and Their Properties

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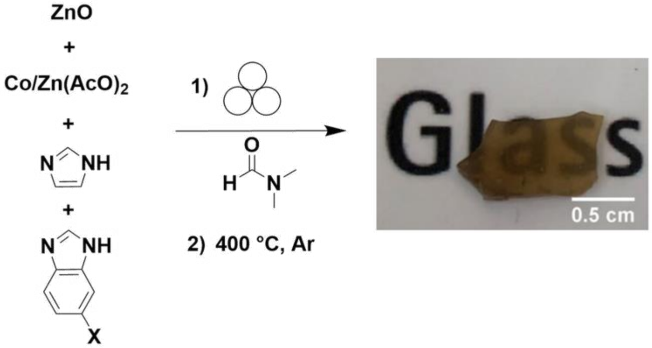
Abstract Text: Metal–organic frameworks (MOFs) are hybrid materials which consist of inorganic nodes, or clusters, connected by organic linkers.[1] Recently it has been demonstrated that some MOFs, namely the zeolitic imidazolate framework (ZIF) subclass of MOFs, have a liquid phase and can be melt-quenched to form ZIF glasses. These ZIF glasses are the first new category of glass since the 1970s.[2] The most promising glass forming ZIFs have the cag topology, with imidazole (Im) and benzimidazole (bIm) type linkers. ZIF-62 ($Zn(Im)_{2-x}(bIm)_x$) and TIF-4 ($Zn(Im)_{2-x}(ClbIm)_x$) are especially promising due to their relatively wide thermal working range, ability to form transparent glass monoliths.[3]

Unfortunately large scale production of ZIF glasses is limited by the inefficient production of the crystalline ZIFs, which rely on large volumes of solvents, high reaction temperatures and long reaction times.[4] Here we present a catalytic mechanochemical method to synthesise the glass forming multi-linker ZIF-62 and TIF-4 with minimal solvent usage, zero organic linker wastage, at room temperature in 30 minutes. These mechanochemically produced ZIFs can be melt quenched to produce glass ZIFs as per the materials synthesised via solvothermal methods. [5]

ZIF-62 and TIF-4 are Zn based ZIFs, however mixed-metal varieties of these materials can be produced using the catalytic mechanochemical method. By employing a Co salt catalyst/metal source into the reaction, up to 20% inclusion of Co into ZIF-62 can be achieved.[5] By introducing Co into the ZIF-62, one can affect the colour of the glass, as well as the melting point of the crystalline material.

We extend this work to produce ZIF-62 and TIF-4 with varying organic linker content, in order to investigate the relationship between chemical composition, and physical properties of the resulting ZIF glasses. The mechanochemical method allows for direct control over the ratio of organic linkers in the crystalline MOFs produced, which is then maintained in the resulting glasses. This allows relationships to be drawn between the organic content of the ZIF glasses, and physical properties such as: melting point/glass transition temperature, hydrophobicity, refractive index and thermal conductivity.

Image 1:



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New Synthetic Methods and Post-Synthetic Modification|MOFs/Organic materials

FEZA21-OR-112

Synthesis and postsynthetic modification of flexible scandium metal-organic frameworks

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Abstract Text: Metal-organic frameworks (MOFs) constructed using trivalent metals have been thoroughly investigated since their first reports by Férey in 2002**.**[1] Their unprecedented flexibility has given rise to their use in many applications such as gas storage, catalysis and drug delivery. Scandium MOFs (Sc MOFs) however, have developed at a much slower rate than their M^{3+} counterparts such as iron and chromium.

The solvothermal synthesis of Sc MOFs can yield both an $[M_3(\mu_3\text{-}O)(COO)_6]$ cluster or chains of corner sharing scandium centres, among several other secondary building units (SBUs).[2] The synthesis can often be tuned to bias one SBU over the other and an approach we have used to do this is called coordination modulation – addition of monotopic ligands to MOF self-assembly – and this methodology has been used to control phases and crystallinity during MOF synthesis. Alongside this, solvent effects have also played important roles in the synthesis of Sc MOFs. Herein, we present the role that dimethylformamide (DMF) and dimethylacetamide (DMA) play during the modulated synthesis. DMA has exhibited a preference to form the trimer cluster, where it can coordinate to the SBU, often producing a different topology compared to syntheses in DMF.

A range of thermally stable Sc MOFs containing alkene and alkyne moieties within the linkers have been prepared and characterised, in order to better understand their flexibility, porosity and stability to post-synthetic modification (PSM), namely bromination. The latter is possible due to the reactive unsaturated carbon bonds in the ligand. Since 2009, minimal work has focused on the post-synthetic bromination of integral, non-terminal unsaturated carbons and as such scandium systems with extended linkers are investigated here.[3] The stereoselective bromination of both bulk microcrystalline and single-crystal phases has been carried out for a range of materials, and fully quantified in MIL-88A(Sc), where quantitative conversion of the alkene has been observed, with retention of the overall framework. Using single crystal X-ray diffraction, a significant contraction of the crystallographic *c* axis can be seen, while the *a* and *b* axes elongate slightly. Similar mechanical contraction has been reported by Marshall *et al.* using inflexible zirconium MOFs.[4] We will detail how PSM affects gas uptake and overall surface area of these frameworks, and show how Sc MOFs can be selectively synthesised and postsynthetically modified to produce novel materials with control over physical properties.

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New Synthetic Methods and Post-Synthetic Modification|MOFs/Organic materials

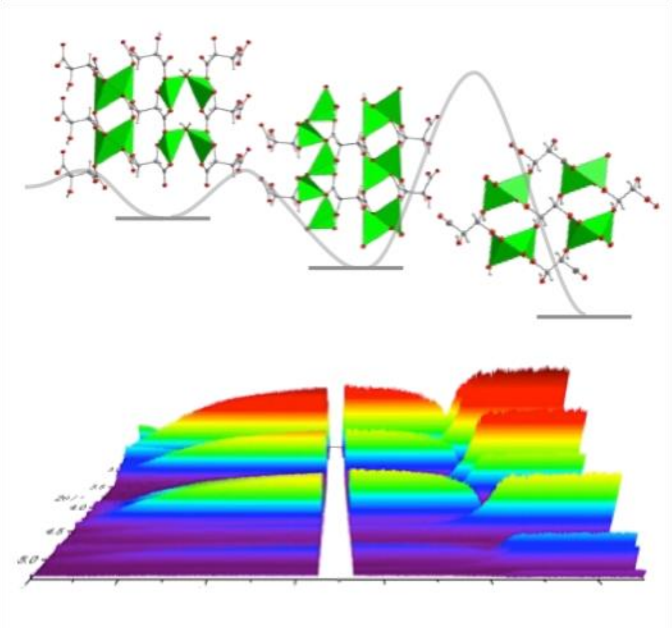
FEZA21-OR-113

In situ insights into the crystallisation of metal–organic frameworks

H. H.-M. Yeung*

Abstract Text: Transformation from the liquid state to ordered solid matter is not only ubiquitous in nature and molecular sciences but it underpins the design and synthesis of many new materials. Recently, *in situ* experiments at central facilities have allowed us to gain insight into the often-surprising processes involved in the crystallisation of metal–organic frameworks. This talk will introduce some recent highlights from our group, including quantifying the energetics of successive polymorphic intermediates (see figure showing *in situ* synchrotron X-ray diffraction data collected at Diamond beamline I12 shows the progressive transformations of metastable intermediate crystalline phases in the lithium tartrate system),[1] uncovering evidence for the existence of pre-nucleation equilibria,[2] and rationalising core–shell heterostructure formation in mixed-component materials.[3]

Image 1:



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New Synthetic Methods and Post-Synthetic Modification|MOFs/Organic materials

FEZA21-OR-114

Selective photochemical postsynthetic reactions of metal-organic frameworks containing the benzophenonedicarboxylate linker

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Abstract Text: Metal-organic frameworks (MOFs) are of interest for a variety of applications like catalysis, gas storage and separation, sensing, energy storage and conversion or biomedicine. To fully exploit the potential of these materials, the structure and the properties of a MOF should be finely tuned to the specific intended application. Generally, MOFs are well prepared to allow for this fine-tuning, as they possess a modular construction from metal oxide nodes and organic linker molecules which allows the introduction of various properties by deliberately choosing the metal and the linker molecule. However, certain specific combinations of properties are difficult to elaborate due to the rather harsh synthesis conditions employed during synthesis. Especially, some desired functionalities which can be placed at the organic linker molecules may be too sensitive to withstand the synthesis procedure. On the other hand, the shaping of MOFs, for example the formation of nanoparticles or thin films, is another important task. For many shaping processes, it would be advantageous if the surface chemistry of a MOF, which regulates for example its dispersibility, could be changed selectively without affecting the pore system. Postsynthetic modification of a MOF can be used to meet both these challenges, the introduction of sensitive functionalities and the modification of the surface chemistry. Here, we describe a specific class of postsynthetic reactions, namely the photochemically induced modification of MOFs containing benzophenonedicarboxylate (bzpdc) as linker. Upon excitation by irradiation with UV light, the benzophenone moiety forms a ketyl radical which then reacts with practically any C-H bond of an organic molecule, allowing for a versatile modification of the MOF structure. Several benzophenonedicarboxylate MOFs have been described in the literature, and photochemical postsynthetic modifications have been described for the Al-bzpdc-MOF (CAU-8)1 and the Zr-bzpdc-MOF.2-3 The latter MOF features quite narrow and corrugated pores, and larger reactant molecules cannot readily diffuse into it.2 Therefore, there is a size discrimination,3 and by the choice of larger reactants, the surface of MOF particles can be modified selectively. For example, we have shown that by the reaction with decane or with polyethylene glycol, MOF particles can be selectively dispersed in an organic solvent or in water, respectively.2 The possibilities to engineer the light with which the photoreaction is initiated, for example by using lasers, should open up further selective modification reactions. 1. H. Reinsch, M. Kr�ger, J. Marrot, and N. Stock. Inorg. Chem. 2013, 52, 1854−1859; H. G. Baldovi, M. Kr�ger, H. Reinsch, M. Alvaro, N. Stock and H. Garcia, J. Mater. Chem. C 2015, 3, 3607–3613. 2. A. Mohmeyer, A. Schaate, B. Brechtken, J. C. Rode, D. P. Warwas, G. Zahn, R. J. Haug and P. Behrens, Chem. Eur. J. 2018, 24, 12848–12855. 3. A. Mohmeyer, M. Sch�fer, A. Schaate, S. Locmelis, A.M. Schneider, P. Behrens, Chem. Eur. J., accepted.

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New Synthetic Methods and Post-Synthetic Modification|MOFs/Organic materials

FEZA21-OR-115

Selective Cobalt precipitation for the synthesis of precursors for cathode materials of li-ion batteries

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Abstract Text: Due to the increase in energy storage for consumer electronics, stationary application and above all for electrical vehicles, the manufacturing of Li-ion batteries has dramatically increased in the past few years. Unfortunately, cathode materials still often use cobalt, and consequently, an increase of 10% per year of the world's cobalt consumption has been observed. Li-ion batteries represent 60% of the use of extracted cobalt today (more than 80% expected in 2030), which is classified as a critical material since 2011 by the European Commission. Battery grade cobalt is produced by only few countries. 60% is provided by the Democratic Republic of Congo. In order to avoid reliance on cobalt supplying, European industry should have to develop alternative solution.

We present here a new way to extract cobalt from a solution of battery-waste materials. Through a one-step process, it is possible to recover the cobalt, selectively, in a solution composed in majority of cobalt, nickel and manganese.

The goal of the process is to form a cobalt-based Metal Organic Framework compounds (MOF) from a multi-metals based solution. The contact of a well-designed ligand with model multi-metallic solution of nickel, manganese and cobalt, under specific conditions, creates a precipitate, which is recovered by centrifugation or filtration. The XRD analysis of the resulting material demonstrates a crystalline structure, and its ICP analysis shows up to 99% of cobalt composition of the metallic nodes of the material. The same process with a real battery waste solution enables the formation of a precipitate made of 94% of cobalt (among the metallic centers).

The resulting MOF can be used as a precursor for synthetizing cathode materials. In order to complete the described closed-loop concept, it is indeed possible to assemble a coin-cell from those products. The well define crystalline structure of the MOF makes them suitable for other industrial application, such as separation or catalysis (open-loop concept).

We are focusing on better understanding of this selectivity process. Density Functional Theory (DFT) calculations are performed, as a tool to evaluate the energy of the different complexes in solution at all states of the nucleation and growth of the MOF. Moreover, the ligand used can form a MOF with each of the metals present in solution. Some nickel and manganese phases (more or less soluble) are involved during the process as a function of the reaction conditions. Identifying their nature and formation is another axis for the understanding of the presented work. Modelling these phenomena could help to determine the reaction that occurs, how the selectivity happens, and why the growing material is made of cobalt only (no other metal).

New Synthetic Methods and Post-Synthetic Modification|MOFs/Organic materials

FEZA21-OR-116

MOF-74(M) films obtained through vapor-assisted conversion - impact on crystal orientation and optical properties

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Abstract Text: Metal-organic frameworks (MOFs) are composed of inorganic nodes that are connected by rigid organic building blocks forming highly crystalline and porous frameworks.[1] Based on their crystalline nature, featuring well-defined pore spaces, tunable chemical compositions and high surface areas, MOFs are intriguing candidates for applications such as gas storage and separations, chemical sensing and optoelectronics. Prominent candiates are materials based on the MOF-74 topology, which have attracted much interest in recent years due to their tunable pore apertures, high surface areas and electrical conductivity.[2] For the implementation of MOFs in a variety of device-based applications, their synthesis as defined and highly crystalline thin films on various substrate types is of paramount importance.

Here, we present the synthesis of highly crystalline thin MOF-74(M = Zn^{2+}, Mg^{2+}, Ni^{2+}, Co^{2+}) films by vapor-assisted conversion (VAC).[3,4] MOF-74 is constructed with 2,5-dihydroxyterephtalic acid ligands, which are connected into honeycomb-like structures through coordination of divalent metal ions. MOF-74(M) thin films were grown on bare glass, quartz, gold and silicon surfaces, featuring high crystallinity, crystal orientation, and average thicknesses of 500 nm. By applying a modulator synthesis approach, oriented MOF-74(Zn) films, with the crystallographic *c*-axis of the MOF crystallites oriented horizontally to the surface, were obtained on all substrates. In contrast, highly crystalline MOF-74(Mg) was grown on glass and gold substrates with the crystallographic *c*-axis aligned orthogonally to the surface. Moreover, randomly oriented highly crystalline MOF-74(Co) and MOF-74(Ni) films were synthesized on glass, quartz, gold and silicon. The pore accessibility of the obtained films was examined by means of krypton sorption measurements, revealing permanent and accessible porosity, reaching a BET surface area of 975 cm^2/cm^2 for MOF-74(Mg). Furthermore, the photophysical properties of the MOF-74(M) films were studied by means of UV-Vis spectroscopy, steady-state and time-resolved photoluminescence spectroscopy and confocal photoluminescence mapping.

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Novel Materials and Structural Methods|MOFs/Organic materials

FEZA21-OR-117

Synthesis and Characterization of ZnAPO/SAPO-58 and ZnAPO-63 with New Zeotype Topologies

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Abstract Text: Recently, we have been interested in the dearth of high charge density (HCD) MeAPO, SAPO and MeAPSO molecular sieves (Me = Zn, Co, Mg, and Mn). Starting with the simple structure directing agents (SDAs) diethyldimethylammonium (DEDMA) and ethyltrimethylammonium (ETMA), we previously prepared MeAPO/SAPO-67 (LEV) with both SDAs, while increasing OH^-/H_3PO_4 led to MeAPO/SAPO-57 (AFV) and MeAPO/SAPO-59 (AVL) in the DEDMA and ETMA systems, respectively. These ABC-6 net topologies exhibit two dimensional 8-ring pore systems.[i] Further increase of OH^-/H_3PO_4 moves the reactions into the Charge Density Mismatch (CDM) region where these SDAs require supplemental alkali to stabilize three-dimensional HCD SAPO and MeAPO species such as SAPO-69 (OFF), SAPO-79 (ERI), PST-16 (CGS) and PST-17 (BPH) in the ETMA/K^+ and DEDMA/K^+ systems, where the chemistry and structures of SAPO and MeAPO systems diverge.[ii] Between these two charge density regimes, we now report the isolation of ZnAPO/SAPO-58 and ZnAPO-63, both of which exhibit new zeotype topologies.

Treatment of the DEDMA-based reaction mixture that gives ZnAPO-57 (AFV) with the diquat 1,3-bis(trimethylammonium)-2-hydroxypropane (bTMAiPr) yields the new zeotype ZnAPO-58. The highly crystalline product exhibits a Zn-rich composition, $N_{0.51}Zn_{0.41}Al_{0.56}P$, compared to ZnAPO-57. ZnAPO-58 crystallizes in the space group $P2_1$, a = 9.1606 Å, b = 14.5835 Å, c = 9.1153 Å, ß = 79.817°. Solution of the structure shows ZnAPO-58 has a two-dimensional 8-ring pore system in the *a-c* plane and interrupted 12-ring pores along the *b*-axis. The interrupted structure is responsible for the excess bTMAiPr/Zn content as well as for terminal P-OH and Al-OH that reside in this pore. ZnAPO-58 was also prepared using TPAOH or TEAOH instead of DEDMA with both bTMAiPr or the cyclic diquat N,N,N'N'-tetramethyl-N,N'butano-1,2-ethylenediammonium dibromide as supplemental SDAs, for which in the latter case, the structure was also solved. SAPO-58 was prepared in both synthesis systems, making this one of the most highly substituted systems in which both ZnAPO and SAPO compositions can be prepared.

Optimization of the Al-Zn stoichiometry in the original DEDMA/bTMAiPr synthesis led to the crystallization of ZnAPO-63, yielding the composition $N_{0.38}Zn_{0.39}Al_{0.62}P$ in the monoclinic crystal system $P2_1/n$, with a = 9.8690 Å, b = 18.8482 Å, c = 9.3993 Å, ß = 118.65°. The structure of ZnAPO-63 also exhibits a two-dimensional 8-ring pore system in the *a-c* plane like the ZnAPO-58. The chemistry, structure and properties of ZnAPO/SAPO-58 and ZnAPO-63 will be presented, including how they fit in with the HCD MeAPOs and SAPOs mentioned above.

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Novel Materials and Structural Methods|MOFs/Organic materials

FEZA21-OR-118

High-throughput structure prediction of metal-organic cages

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Abstract Text: Molecular porous materials are a broad class of materials whose functions are closely related to their structures and their intrinsic porosity. We have developed the supramolecular toolkit (*stk*), which is an efficient and general structure prediction software for the discovery of molecular materials, including porous cages, polymers, macrocycles, rotaxanes and covalent organic frameworks, with targeted structures and properties.[1] We have applied *stk* alongside many computational methods (including machine learning, evolutionary algorithms and high-throughput screening) towards the structure and property prediction of porous, molecular materials.[2-4] Herein, we present the extension of *stk* to handle the construction of metal-organic cages (MOCs). We show that *stk* can handle the broad diversity of metal-ligand chemistries and supramolecular topologies present in the MOC literature. In particular, we apply *stk* to develop a high-throughput screening workflow for new *cis*-heteroleptic $M_2L'_2L''_2$ MOCs. Heteroleptic MOC assemblies offer great opportunities for the precise tailoring of the shape and chemistry of the intrinsic pore of cage compounds.[5,6] Firstly, we use *stk* to build a combinatorial library of approximately 250 ditopic, pyridine ligands. Using cheminformatic tools and the available experimental data, we devise a ligand-based screening approach for candidate ligand pairings that may form stable *cis*-heteroleptic assemblies. Our approach screens ligand pairs based on their flexibility, which we found to discriminate the few known experimental cases, and their geometrical match. We then use *stk* to build the proposed heteroleptic cage and competing homoleptic cages (based on common Pd_nL_{2n} topologies) from the top candidate pairs of ligands. We attempt to apply geometrical measures (instead of expensive computational calculations) to determine whether a candidate heteroleptic cage is stable and likely to outcompete the relevant homoleptic species. Finally, our computational screening will directly drive experimental endeavours towards the discovery of new *cis*-heteroleptic cages.

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Novel Materials and Structural Methods|MOFs/Organic materials

FEZA21-OR-120

Structure prediction of amorphous Metal-Organic Frameworks

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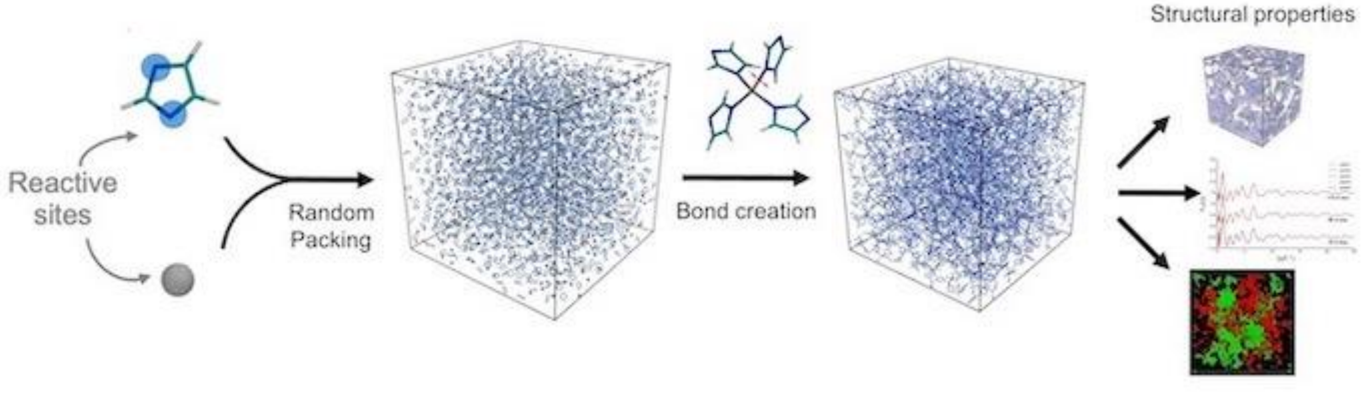
Abstract Text: Metal-organic framework (MOF) glasses and amorphous MOFs (*a*MOFs) are a new class of non-crystalline hybrid materials that combine porosity with the advantages of glasses, such as the possibility to be shaped into bulk morphologies, which makes them good candidates as membrane materials for gas separation.[1] However, due to their lack of structural long-range order, they are much more challenging to characterise compared to their crystalline counterparts, making their structure-property relationships difficult to discover. In this scenario, molecular simulations can help by providing structural models and complementary information derived from an atomistic level understanding. Using a computational approach that we initially applied to the structure prediction of porous polymers,[2,3] we investigated the structure of the amorphous zeolitic imidazolate framework-4 (*a*ZIF-4), a prototypical glass forming MOF.[4] In this case, we could successfully reproduce experimentally observed properties, including *a*ZIF-4 porosity. Notably, our approach does not use any experimentally derived data as a target property for the structure construction, giving us the possibility to predict the structure of hypothetical *a*MOFs that have not been synthesised yet in the lab. We have now expanded this structure prediction approach to other archetypical MOF chemistries, whose amorphous structures have never been computationally studied. Herein, we present models for *a*MIL-100(Fe), FeBTC and *a*UiO-66. We found good agreement with experimental scattering data and porosity measurements, validating our amorphous structure prediction approach. Furthermore, we used our models to understand, at a molecular level, the influence of the degree of defects and disorder on the final structure of *a*MOFs, and how these properties can be modulated experimentally. Interestingly, we found that increasing the amount of defects in MIL-100 brings about a collapse of the amorphous structure reducing the overall porosity. This structure prediction approach opens the possibility to outline design rules for *a*MOFs, allowing us to suggest new promising *a*MOF structures with properties tailored for specific applications.

Image 1:



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Novel Materials and Structural Methods|MOFs/Organic materials

FEZA21-OR-121

Discovery of Synthesisable Organic Materials

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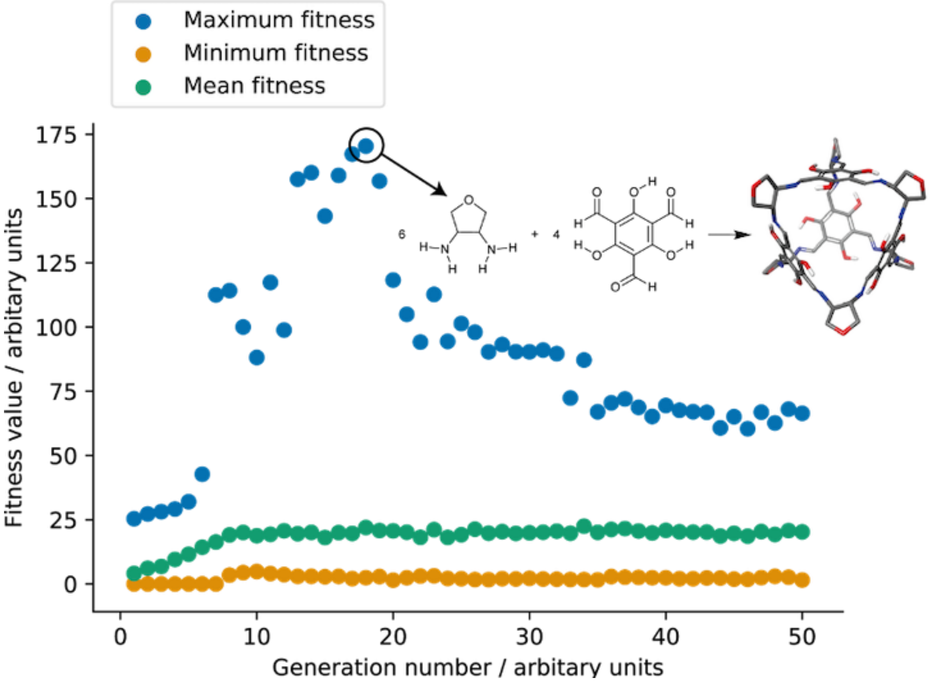
Abstract Text: Porous organic cages (POCs) have been discovered as a possible alternative material for molecular separations, catalysis and sensing applications.[1] However, due to the diverse number of potential precursors and reactions that can be used to form a novel POC, it can be time-consuming and computationally expensive to screen a large number of possible candidate molecules.[2] Despite being able to predict materials with exceptional properties, it is often difficult to predict whether it is possible to synthetically realise a potential candidate compound. Additionally, molecules that are more difficult to synthesise could result in extremely useful properties. In the field of drug discovery, machine learning techniques have been able to readily distinguish between synthesisable and unsynthesisable molecules, accelerating the drug discovery process.[3]

Using synthetic accessibility scoring techniques, we aimed to incorporate a screening technique for synthetically viable molecules into our existing high-throughput POC screening workflow, eliminating compounds unlikely to be experimentally realised. We used the previously reported materials design software, *stk*,[4] in conjunction with its evolutionary algorithm,[5] to explore the chemical space of possible candidate compounds. Precursors from a diverse chemical database were combined in pre-defined topological configurations, the lowest energy conformation for each structure was identified, and its properties screened. Individual structures were assessed using a fitness function, tailored to promote POCs with a permanent internal cavity, with high shape persistency.

We found that incorporating a synthetic accessibility scoring function into the fitness function favoured synthetically accessible POCs (Figure 1), bridging the gap between computational screening and experimental synthesis of POCs. By optimising synthetic accessibility as an independent property, candidates exhibiting exceptional properties but were more difficult to synthesise were not eliminated. Furthermore, we tried to reproduce the chemical intuition of an expert organic chemist, attempting to model the decision process used when selecting potential precursor molecules. By redefining synthetic accessibility as a classification problem, we were able to create a random forest model that classified molecules as synthetically accessible or inaccessible. This screening workflow is also not limited to POCs, as it can be extended to other materials designed using a similar bottom-up, modular approach.

Image 1:



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Novel Materials and Structural Methods|MOFs/Organic materials

FEZA21-OR-122

The Structure, Synthesis and Properties of the Carboxyethylphosphonate Metal–Organic Framework BIRM-1.

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Abstract Text: Metal–organic frameworks based on phosphonate linkers are a sometimes neglected area of MOF research. The use of a phosphonate-based linker rather than more traditional carboxylate or nitrogen-containing linker compounds has both benefits and drawbacks. The presence of 3 coordinating oxygen atoms compared to 2 in carboxylates allows for both an increase in stability of the structure and an increase in possible geometries leading to greater potential for new and interesting structures. Conversely, phosphonates have a tendency to form as dense structures *via* rapid nucleation making growth of single crystals and subsequent structure solution difficult.[1]

To address some of these issues, we have developed the synthesis of a novel carboxyethylphosphonate-based MOF. Using a linker with both a phosphonate and carboxylate group enables some of the benefits of phosphonates to be exploited and some of the drawbacks to be alleviated.

The first product of this work is a zinc carboxyethylphosphonate MOF (BIRM-1) with the formula $(NH_4)_2[Zn_2(O_3PCH_2CH_2COO)_2]\cdot 5H_2O$. This material has an anionic framework allowing for the inclusion of cations and facilitating ion exchange for a range of different metal ions, a property exhibited only by a minority of MOFs.[2,3] BIRM-1 was produced *via* a hydrothermal reaction between zinc nitrate, urea, tetraethylammonium bromide and carboxyethylphosphonic acid. The urea plays an interesting dual role in the reaction both as a base to deprotonate the linker and as a source of ammonium cations *via* thermal decomposition. The use of urea rather than directly adding a stronger base allowed for a slower change in pH, promoting the growth of large single crystals. The ammonium ions have successfully been exchanged for a range of different cations including Li^+, Na^+, K^+, Cs^+, Mg^{2+}, Mn^{2+} and Co^{2+}, which allows for potential applications such as improved gas storage or waste water remediation.[2]

This synthesis route is highly sensitive to temperature with a difference of just 10˚C resulting in the formation of 4 different phases. Alternative methods were explored and it was found that BIRM-1 could be synthesized very rapidly at room temperature and pressure, the trade-off being that large crystals were not formed. By employing different bases, forms which had previously been produced *via* ion-exchange could also be accessed directly. This new procedure under ambient conditions offers the possibility of developing a flow synthesis route, enabling relatively easy scale-up compared to a hydrothermal batch process.

BIRM-1 contains water molecules within the pores and channels of the framework. Their presence and removal result in interesting properties such as proton conductivity and reversible amorphization that may also be exploited in future applications.

Image 1:

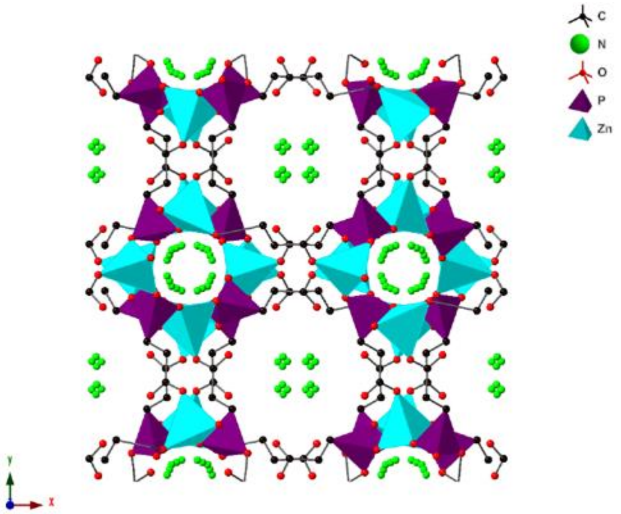

Image 2:

$$CO(NH_2)_2 \longrightarrow NH_4CNO$$

$$NH_4 + 2H_2O \longrightarrow (NH_4)_2CO_3$$

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Physical Properties and the Role of Defects

FEZA21-OR-123

Correlated Linker Disorder in Metal-Organic Frameworks

E. Meekel*

Abstract Text: Correlated Linker Disorder in Metal-Organic Frameworks

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The first developments on metal-organic frameworks, or MOFs, were made approximately four decades ago, marking the discovery of a novel class of porous materials. Initially thought to be ordered and truly crystalline, there is now an increasing realisation that defects and disorder are prevalent in MOFs, and that nontrivial arrangements can be important in physical properties [1]. Though, disorder in MOFs does not necessarily imply randomness. In fact, depending on the interactions between components, MOF structures can exhibit short-range order and long-range disorder simultaneously. This is what we refer to as correlated disorder [2]. Thorough understanding is achieved through investigation of the interactions involved in causing these states, with the aim of controlling physical properties via their manipulation.

Generally, there are three types of disorder observed in MOFs: vacancy defects, compositional disorder, and orientational/conformational disorder [3]. The latter forms the focus of this project. A key factor is the distinction between molecular point symmetry (*i.e.* the local structure) and that of the corresponding position in the lattice (*i.e.* the average structure). Namely, molecular components are arranged on a lattice of which the geometry is determined by that of the MOF, giving control over the molecular orientational degrees of freedom [4]. Since MOF geometry is often highly symmetric, lowering the symmetry of nodes and/or linkers can enable targeted design of correlated conformational disorder.

In this work, correlated disorder is introduced to the highly symmetric (hypothetical) parent framework ZnO_4(BTC) (BTC = benzene tricarboxylic acid) by reducing the linker symmetry from D_{3h} to C_{2v}, giving ZnO_4(1,3-BDC) (BDC = benzene dicarboxylic acid). The resulting linker disorder is characterised via diffuse scattering observed in single crystal X-ray diffraction (SCXRD) patterns, 3DΔ-pair distribution functions (3DΔ-PDFs), and Monte Carlo code. Ultimately, we want to understand how to control defective structures in MOFs to optimise their properties, enabling utilisation in real-life applications.

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Physical Properties and the Role of Defects|MOFs/Organic materials|Poster

FEZA21-OR-124

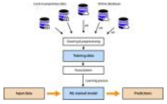
Systematic exploration of physical properties of nanoporous materials properties: combining quantum calculations, classical simulations, and machine learning

F.-X. Coudert*

Abstract Text: The past few years have seen a rapid increase in the use of machine learning (ML) approaches to the fields of chemistry and materials science, in particular in the prediction of physical and chemical properties of existing and novel compounds. Databases of experimental structures—in particular, crystalline structures—continue to grow at a steady pace and are complemented with larger and larger databases of physical and chemical properties. However, these databases are limited in their

We present here several examples of a multi-scale computational approach to this problem, by combining the existing tools of theoretical chemistry (i.e., quantum chemical calculations and classical molecular simulations) with statistical learning approaches. We show how these have been integrated together in our group and allow not only the prediction of properties, but also a deeper understanding of the structure/property relationships that can provide chemical insight. We also highlight the typical limitations of these approachs, in terms of quality and size of datasets, as well as accuracy and reproducibility of the methods. We highlight these effects on three different types of properties of nanoporous materials: (i) gas adsorption and separation; (ii) mechanical behaviour; (iii) thermal properties.

Image 1:



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Stimuli Responsive Behaviour and Emerging Properties

FEZA21-OR-125

New insight into the thermoresponsive behaviour of MIL-53 MOFs revealed by in-situ single crystal X-ray diffraction

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Abstract Text: Metal-organic frameworks (MOFs) are porous inorganic-organic hybrid materials possessing exciting properties and potential applications in fields such as gas adsorption and catalysis.[1] One such property is stimuli driven framework flexibility. The MIL-53 family is a widely studied group of flexible MOF that typically show a range of stimuli dependant framework structures ranging from contracted narrow pore (np) to intermediate (int) and open large pore (lp) phases.[2] These frameworks consist of 1-dimensional trivalent metal ion-containing chains bridged by terephthalate (BDC) linkers, as shown in Fig. 1. Great variability in the stimuli dependant phase change response has been observed by changing the trivalent metal in the material. For example [Cr(OH)(BDC)] and [Al(OH)(BDC)] both show a framework expansion from the np phase to the lp phase with increasing temperature,[2] while [Fe(OH)(BDC)] does not show a full expansion to a lp phase upon heating and remains in a np phase. Variable temperature studies on MIL-53 frameworks are often incomplete and have typically been performed using polycrystalline samples. Single crystal studies of such phenomena are advantageous as they yield accurate structural information and allow the study of the phase change of one crystal only. In this work the thermoresponsive behaviour of Ga-MIL-53 [Ga(OH)(BDC)] is investigated using *in-situ* variable temperature single crystal X-ray diffraction (VT SCXRD) to provide new insight into the behaviour of this family of flexible MOF.

Single crystals of [Ga(OH)(BDC)]·0.85C_5H_5N (C_5H_5N = pyridine)[3] and [Ga(OH)(BDC)]·H_2O were prepared and *in-situ* VT SCXRD data were collected from both samples. lp-[Ga(OH)(BDC)]·0.85C_5H_5N (see Fig. 1a) transforms to lp-[Ga(OH)(BDC)] (see Fig. 1b) upon heating under nitrogen at 473 K, which then transforms to the np-[Ga(OH)(BDC)] at 300 K upon cooling (see Fig. 1c). This sharp thermally driven phase transition has not been identified for this compound and interestingly occurs at a much higher temperature than for [Al(OH)(BDC)].[4] np-[Ga(OH)(BDC)] remains in this form upon slow heating (360 K/h) to 500 K. int-[Ga(OH)(BDC)]·H_2O is found to exhibit a previously unreported, and energetically, lower structure at 150-350 K (see Fig. 1d) than has been reported for analogous MIL-53 compounds. Slow heating (360 K/h) of this compound shows that it transforms to np-[Ga(OH)(BDC)] at 300-350 K and remains as this phase upon heating to 500 K. This contrasts with the results reported for a polycrystalline [Ga(OH)(BDC)]·H_2O sample for which np- and lp-[Ga(OH)(BDC)] are present between 448 – 493 K.[5, 6] Interestingly, if the crystal of int-[Ga(OH)(BDC)]·H_2O is placed directly under a heated N_2 stream at 500 K then it rapidly converts to lp-[Ga(OH)(BDC)] demonstrating that flash heating can be applied successfully to induce transitions between the phases of MIL-53. Density functional theory (DFT) calculations support the findings of the VT SCXRD studies, and suggest the importance of non-covalent hydrogen bonding and π-π stacking interactions in stabilising the np phase over the lp phase.

Overall, this work demonstrates that in-situ VT SCXRD can provide new insight into the structure and behaviour of the flexible MIL-53 family of MOFs and demonstrate an unreported method to achieve transformations between the phases of the family.

Image 1:

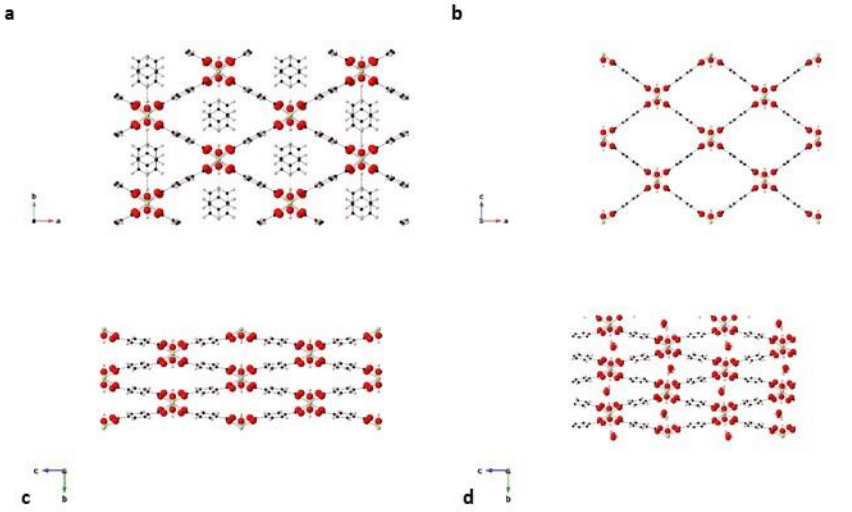

Fig. 1 The crystals structures of (a) $[Ga(OH)(BDC)]\cdot 0.85C_5H_5N$, (b) lp-$[Ga(OH)(BDC)]$, (c) np-$[Ga(OH)(BDC)]$ and (d) int-$[Ga(OH)(BDC)]\cdot H_2O$. Ga=green, O=red, C=black, H= pink.

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Stimuli Responsive Behaviour and Emerging Properties

FEZA21-OR-126

Emergence of topologically protected phases in framework materials

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Abstract Text: Topologically protected states are ideal candidates for memory storage applications due to the preservation of information contained in their topological charge [1, 2]. A particular interest has been in magnetic topologically protected phases, such as skyrmions, as they are easily manipulated with a magnetic field [3]. However, accessing these states for industrial applications can prove challenging as the temperatures required for the formation of spin textures typically occur below ~ 30 K [4] and topological charges only manifest within a small regime of ~ 2-3 K within this range [5]. This low energy scale poses severe challenges for experimental studies and practical applications of magnetic textures.

The formation of magnetic textures relies on competing local interactions arising from the chirality of the underlying magnetic lattice and ferromagnetic interactions between spins, causing them to order on the mesoscopic scale. Although the interactions leading to topologically protected magnetic phases are well characterised, the number of chemical families known to support these textures remains remarkably small due to the difficulty of engineering the interactions [6]. Moreover, most topologically protected phases require extreme conditions such as low temperatures or high magnetic fields. Therefore finding more experimentally accessible phases could increase our understanding of how they may be manipulated, and opens potential pathways to producing low energy spintronics.

The search for new materials that could host topologically protected phases relies heavily on the chirality of the lattice. Whilst chirality is rare amongst ferromagnetic metals, it is commonplace amongst metal organic frameworks (MOFs). Manipulating MOF topology is routine in structural chemistry [7]. In fact there are now a number of well-established strategies for synthesising chiral MOFs [8,9]. Although magnetic interactions are notoriously weak in MOFs [10], the intermolecular interaction between molecules within pores can be strong—such is the basis of the 'crystalline sponge' concept [11,12]. Moreover, the pore networks of chiral MOFs are of course themselves chiral [13], and so the interactions between guest molecule confined within these pores automatically include an important component in producing topologically protected phases. So guest-loaded chiral MOFs are perhaps surprisingly well placed to support topologically nontrivial states, built on collective orientational degrees of freedom—rather than the more usual magnetic order. We therefore pose the question: might MOFs be capable, in principle, of harbouring orientational skyrmions?

In this study [14], we aim to answer this question in three stages. First, we establish a simple interaction model that relates the problem of orientational order in chiral MOFs to that of magnetic order in materials containing skyrmionic states. Second, we perform a series of classical Monte Carlo simulations in order to establish the phase behaviour of our interaction model, evidencing a number of accessible topologically nontrivial phases (Image 1). Third, to determine the extent that real materials might exhibit the thermodynamic behaviour produced by our Hamiltonian, we employ a mixture of density functional theory calculations and ab initio molecular dynamics simulations on a candidate MOF, $[Al(N_3)_3](C_6H_6)$ (Image 2a), and track the energetics of the structure as a function of strain and temperature. We find that the energetics of the material can be well described by our coarse grained model (Image 2b), implying that metal organic frameworks may have the potential to harbour complex topological phases.

Our study focuses on the propensity of these phases in metal organic frameworks. However, in principle, these phases could exist in a whole host of chiral frameworks including zeolites and covalent organic frameworks.

Image 1:

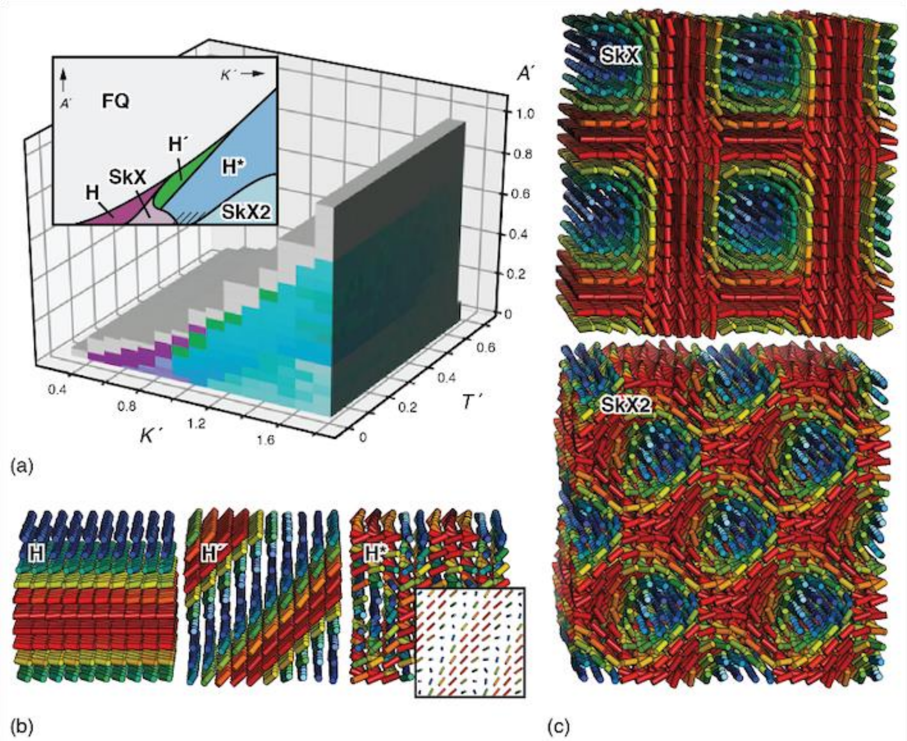
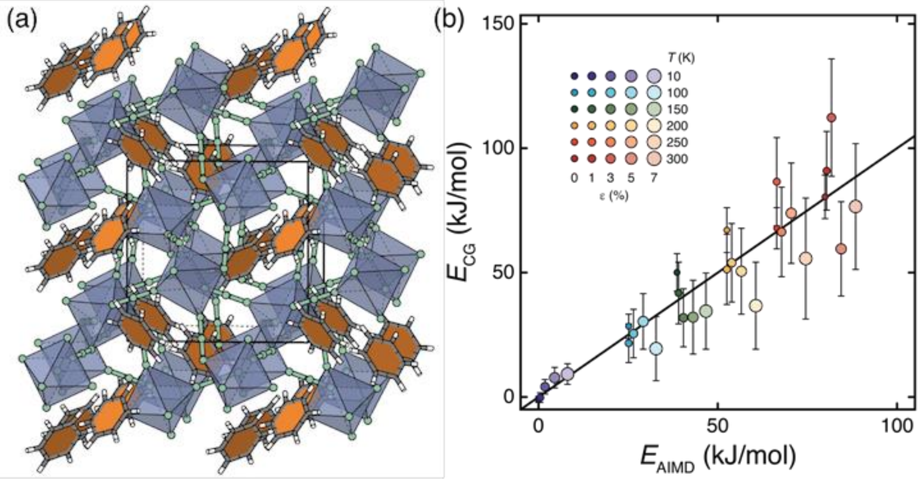


Image 2:



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Stimuli Responsive Behaviour and Emerging Properties|MOFs/Organic materials

FEZA21-OR-127

Investigating the Melting Behaviour of Polymorphic Zeolitic Imidazolate Frameworks

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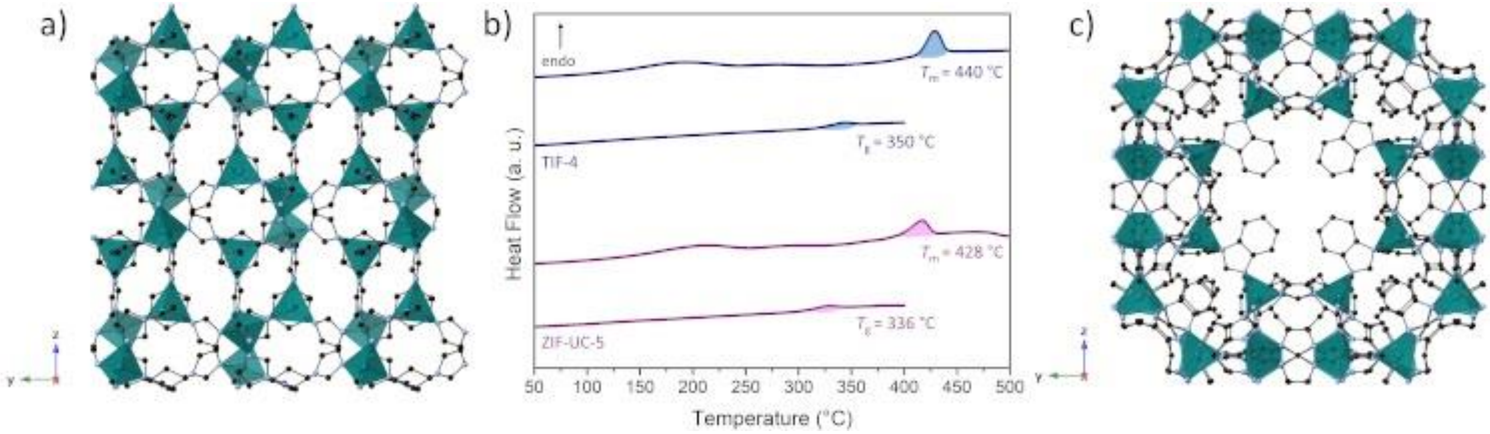
Abstract Text:

Until recently, research in the field of metal–organic frameworks (MOFs) has been dominated by the study of crystalline materials. However, growing interest is being shown towards defective and flexible materials as well as structural transitions from the crystalline to the amorphous state.[1–3] MOFs share much overlap with traditional zeolites. The zeolitic imidazolate framework (ZIF) family in particular adopt many of the same network topologies as zeolites, given that they consist of MN_4 tetrahedra linked through bridging imidazolate ligands.[4] A particularly topical aspect of the physical behaviour of ZIFs is melting, which has been recently discovered.[3] First principles molecular dynamic simulations in conjunction with X-ray total scattering data have revealed that melting occurs through rapid de-coordination of an imidazolate linker from the metal centre followed by re-coordination of a new linker in its place.[5] However, not all ZIFs melt and it is still not well understood how factors such as linker chemistry and crystal structure influence the thermal response of these materials.

To investigate this, a number of ZIFs were selected based on their chemical or structural similarities. TIF-4 and ZIF-UC-5 are structural isomorphs, both containing Zn^{2+} ions, imidazolate and substituted benzimidazolate linkers, crystallising in an orthorhombic *Pbca* space group with the **cag** topology (Fig. 1a).[6,7] However, in TIF-4 the linker substituent is a methyl group whilst in ZIF-UC-5 it is a chlorine atom. Comparison of these materials allowed the influence of linker chemistry to be studied. It was found that the presence of a more electron withdrawing chlorine substituent lowered both the melting and glass transition temperature (Fig. 1b). This provides a promising strategy for the preparation of MOF glasses with more industrially relevant working temperatures.

In contrast, ZIF-76-mbIm contains the same metal ion and organic linkers as TIF-4 but crystallises in a more porous, cubic framework with the *P-43m* space group and the LTA topology and does not melt on its own (Fig. 1c).[4] However, the presence of a small quantity of dense phase impurity in ZIF 76-mbIm can assist melting of the porous framework. This is believed to occur through a phenomenon termed flux melting whereby the dense ZIF first melts and acts as a solvent, facilitating melting of the second framework.[8] This opens up the rich polymorphic landscape of ZIFs to melting by providing a strategy to prepare novel functional glasses from ZIFs that do not melt on their own.

Image 1:



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Stimuli Responsive Behaviour and Emerging Properties|MOFs/Organic materials

FEZA21-OR-128

Fast-Switching Vis-IR Electrochromic Covalent Organic Frameworks

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Abstract Text: Covalent organic frameworks (COFs) are constructed from precisely designed building blocks giving rise to new porous materials with well-defined optoelectronic properties. In two-dimensional COFs, covalently-linked building blocks form sheet-like layers that are π-stacked in the third dimension, creating conductive columns with the ability to incorporate guest molecules.

In our previous study, we presented strongly absorbing 2D COFs by incorporating donor-acceptor-type building blocks into highly ordered frameworks.[1] Here, the combination of electron-rich and -deficient moieties within highly planar thienoisoindigo-based building blocks leads to additional intramolecular charge-transfer transitions at energies well below the fundamental π-π* transition. This strategy paved the way for new intensely colored materials that absorb light throughout the visible and NIR spectral region.

The modular construction principle of COFs enables the tunability of key features by chemically modifying the implemented building blocks, thus extending the field of possible applications. Here, we designed a new series of thienoisoindigo-based COFs to apply them as electrochromic materials.[2] Oriented thin films of these frameworks with their accessible pores extending towards the film surface exhibit intrinsic color changes in response to an external electronic stimulus. Based on their specific composition, our new low-bandgap COFs not only offer strong optical absorption but also fully reversible and highly efficient electrochromic color changes at extremely fast switching times of 0.38 s for the oxidation (coloring) and 0.20 s for the reduction (bleaching).

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Stimuli Responsive Behaviour and Emerging Properties|MOFs/Organic materials

FEZA21-OR-129

Exploration of n-Butane Diffusion in Highly-Flexible Mesoporous Metal-Organic Framework DUT-49 using the Pulsed Field Gradient NMR

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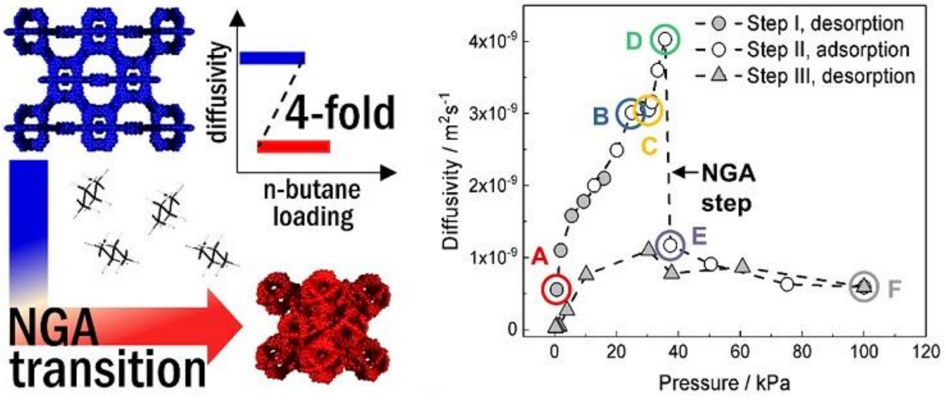
Abstract Text: The recently discovered phenomenon of negative gas adsorption (NGA) in a metal-organic framework (MOF) [1] has initiated a series of experimental and theoretical studies investigating its underlying nature and applicability limits with different gases and under different conditions. To a large extent, these studies have aimed to understand the thermodynamic conditions required for a host-guest system to transform and release gas. Practically, flexible MOFs show in some cases very high selectivity in gas separation, the nature of which still remains is poorly understood.

The obvious role of molecular diffusion in the processes of fluid distribution within this complex and dynamic pore structure has not been investigated until now. One could expect a notable change in the mechanisms of diffusion due to the large change of framework structure (and therefore of a nanoconfinement). Indeed, in the proposed contribution, we report an observed step-like change of *n*-butane diffusivity within the MOF during the NGA-step [2]. The framework contraction has led to a 4-fold decrease in the self-diffusion coefficient with the pressure step of less ~1.5 kPa. This observation was possible due to application of diffusion NMR techniques capable of in situ detection of molecular displacements within MOF crystals combined with molecular dynamics and Monte Carlo simulations. To the best of our understanding, it is the first experimental study performed by means of pulsed field gradient NMR in highly-flexible MOFs.

Furthermore, the obtained results provide a detailed microscopic picture of the pore loadings and demonstrate transformations of diffusion mechanisms upon increase of a sorbate concentration. It has been demonstrated on MOFs, but we believe that these findings are relevant for other systems undergoing a colossal structural modification, in which molecular diffusion in nanoconfined environments is involved, e.g. thermoresponsive membranes, porous liquids and polymers, nanoporous systems for controllable encapsulation and drug delivery.

Image 1:



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Advanced Characterisation and Operando Spectroscopies

FEZA21-OR-130

Advanced characterisation of disordered mesoporous solids

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Abstract Text: Mesoporous solids used in practical applications often possess structural disorder over broad length scales. This disorder strongly affects different properties of the substances confined in their pore spaces, such as their transport characteristic or adsorption properties. Quantifying structural disorder and correlating it with the physical properties of confined matter is thus a necessary step toward the rational use of mesoporous solids in practical applications and process optimization. The present work focuses on recent advances made in the understanding of correlations between the phase state and geometric disorder in nanoporous solids. We overview the recently developed statistical theory for phase transitions in a minimalistic model of disordered pore networks represented by the linear chains of pores with statistical disorder [1]. By correlating its predictions with various experimental observations, we show that this model gives notable insight into collective phenomena in phase-transition processes in disordered materials and is capable of explaining self-consistently the majority of the experimental results obtained for gas–liquid and solid–liquid equilibria in mesoporous solids [2,3]. The potentials of the theory for improving the gas sorption and thermoporometry characterization of porous materials will be discussed. In particular, we will show how the interconnectivity parameter of the pore network can be assessed used the novel approach. As well, the extension of the theory for other networks, rather than the linear pore chains, will be discussed.

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Biomedical Applications

FEZA21-OR-131

Evaluating and Understanding the Performance of MOF- Polymer Composites for Medical Device Applications

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Abstract Text: Storage and delivery of biologically active gases for medical applications are amongst the most exciting potential uses for MOFs. Ni-CPO-27 (a 2,5-dihydroxytherephthalate framework with nickel as its nodes) shows exceptional storage and release properties for nitric oxide (NO)[1], a gas that exhibits anti-bacterial, anti-thrombotic and wound healing properties when delivered in low concentrations.[2] Employing MOFs as storage/release agents permits these advantageous properties to be harnessed by controllably delivering low concentrations of the gas, thus avoiding the toxicity associated with high concentrations. NO-releasing MOFs are therefore potentially very suitable for incorporation into medical devices such as catheters, which are a major cause of Healthcare Associated Infections.

Recent research has endeavoured to embed (meso-)porous materials into polymeric matrices as composites for the purpose of performing gas adsorption and separation.[3] MOF-polymer composite films provide an ideal model for MOF-containing components of potential medical devices, permitting analysis and development of critical properties prior to full device prototyping.

In this study, a series of MOF-polymer composites (containing 5-40 wt% MOF) have been synthesised, successfully loaded with NO and their stability to storage and NO release performance analysed. Intuitively, increasing the MOF loading level in the composites should result in higher concentrations of NO being released, however our results indicate that there is an optimum loading level for peak performance. Using focused ion beam assisted cross sectioning, 3D-reconstruction and SEM imaging we have studied the MOF's distribution throughout the polymer resin to understand this behaviour. We have shown that the concentration of NO released from the surfaces of these MOF-polymer composites can impart antibacterial efficacy. Moreover, this bactericidal activity is sustainable for longer than current commercially available antibacterial catheter coatings.

Image 1:

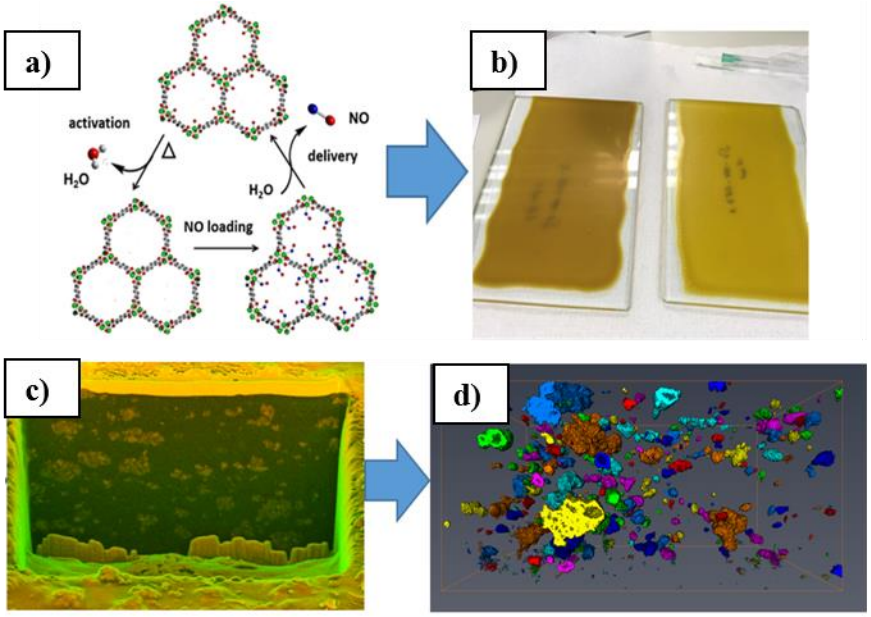

Figure 1: Nitric oxide (NO) sorption and SEM analysis of MOF-polymer composite. a) NO-loading and -release cycle of a typical CPO-27 material; NO is bonded to the open metal sites of the MOF, where its release is triggered by moisture b) MOF-polymer composite film synthesised with two different wt% MOF loadings c) Exposed MOF particles in a cross section of a 10 wt% MOF-polymer composite milled with a focused ion beam (FIB) assisted SEM and d) the 3D rendered volume that the MOF occupies inside the polymeric matrix of a 10 wt% film, each invidual MOF-aggregate is represented with a new colour; data was acquired from a 3D reconstruction FIB-SEM experiment.

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Biomedical Applications

FEZA21-OR-132

Nanosized zeolite Beta based drug formulation for the simultaneous release of silver and sulfadiazine

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Abstract Text: Topical antibacterial treatment is of major importance for burn injuries. An appropriate procedure for such treatment is a formulation containing both silver and sulfadiazine (SD), in practice the combined drug substance, silver sulfadiazine (AgSD). AgSD however, has extremely low solubility in aqueous systems and only slightly better in organic ones. Thus, it cannot be considered as a ‘hydrophobic’ molecule, preferable for topical delivery, permeating fast through the skin lipids. In addition, antibacterial activity develops only by decomposition of AgSD, i.e. by slow dissociation of silver ions under physiological conditions. The above mentioned disadvantages can be overcome by the individual introduction of the two constituents, i.e. silver and the antibiotic sulfadiazine. Nanosized H-Beta zeolite was chosen as drug carrier, because of it peculiar textural properties. Nano-Beta zeolite prepared by freeze-drying method is not composed of monocrystals but clusters of 10-20 nm spherical nanoparticles with hydrodynamic diameter of 280 nm in 5.5 pH buffer solution.

Silver was incorporated into nanosized zeolite H-Beta by mechanochemical method (vibrating ball milling) in an excess amount compared to its ion-exchange capacity. The zeolite was dry mixed with silver nitrate, followed by heat treatment at 520°C in air or in N_2. It was found that by this simple solid-state encapsulation method the exchangeable cation sites were filled with silver ions and the surplus formed 5-20 nm sized silver nanoparticles stabilized on the outer surface or among the voids of zeolite nanoparticles (Fig. 1). FT-IR spectroscopic and thermo-gravimetric results gave evidence for the solid state ion-exchange (SSIE) of Beta zeolite with silver ions. ^{27Al}MAS-NMR investigations revealed that incorporation of silver ions resulted in restoration of tetrahedral Al position, i.e. ‘healing’ of the framework disruptions. The mechanism of SSIE was studied by thermo-gravimetric-mass spectrometric analysis. Detection of evolved NO, NO_2 even at 100°C point towards that contact induced ion-exchange proceeds according to the equation:

$H^+Z^- + AgNO_3 = Ag^+Z^- + HNO_3$.

Sulfadiazine (SD) drug was deposited on AgB and HB zeolite also by vibrating ball milling. Our experiments revealed that Beta zeolite nanoparticles were able to store and release the loaded SD, together with the supported Ag. In pH=5.5 buffer solution almost total release of SD was observed from the parent HB and Ag-containing formulation. Meanwhile, ~25 % of the encapsulated Ag, deposited most probably as ionic silver species, is delivered into the buffer solution (Fig. 2). The prolonged release of SD on AgB suggest that the concomitant presence of Ag and SD influence the release kinetics of both components. The drug delivery system based on SD loaded AgB exhibit significantly improved release properties compared to pure silver sulfadiazine.

The potential of combined antibacterial action of the novel silver-based zeolite-sulfadiazine composite as a drug delivery system has been tested using *Escherichia coli, Staphylococcus aureus, Pseudomonas aeruginosa* and *Streptococcus pyogenes* strains as model. The presence of silver in the developed formulations led to enhanced bactericidal effect on the studied strains.

By applying different amounts of silver precursor compound the nature and size of silver nanoparticles can be controlled, influencing also the bioactivity of the release system.

Acknowledgement

Support of the Hungarian-Bulgarian Inter-Academic Exchange Agreement is gratefully acknowledged.

Image 1:

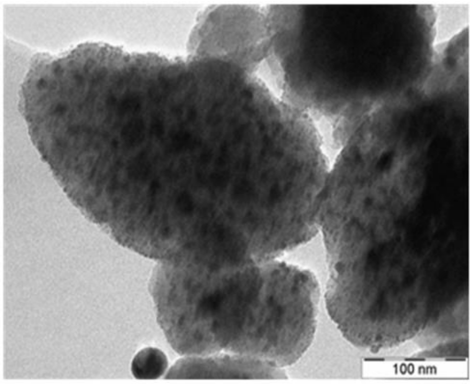

Fig. 1 TEM image of silver Beta zeolite prepared by solid-state encapsulation method

Image 2:

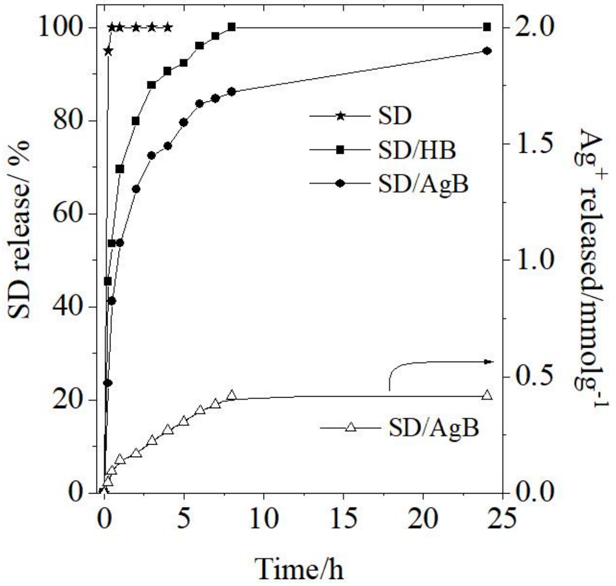

Fig. 2 In vitro release of sulfadiazine and its H-Beta and AgB supported varieties in pH=5.5 buffer solution

Industry Discussion Session

FEZA21-OR-134

The industrialisation process of an ionic liquidic zeolite (ILZ) adsorbent for coal seam gas purification

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Abstract Text: Methane (CH_4) is an important clean energy among fossil fuels. For the same power output, combustion of methane produces less than half CO_2 compared with coal, and nearly no sulphur oxides or particulate matters. Methane also plays a significant role in meeting the Paris Agreement, enabling sustainable energy supply while reducing the carbon emission and air pollution by replacing coals. Therefore, the capture and reuse of CH_4 from low grade gas sources such as coal mine gas, liquified natural gas (LNG) vent gas and biogas, has a critical environmental, social and economic impact. In this regard, materials with high selectivity for CH_4 is preferred. Here we report the roadmap of an initiated industrial separation process from laboratory research (a new porous material named ionic liquidic zeolite, ILZ, 2011), to large scale demonstration (2016) and then industry employment for coal seam gas purification last year (2020). Qualified natural gas products ranging from pipeline natural gas, compressed natural gas and liquefied natural gas were successfully produced through the vacuum swing adsorption (VSA) process using a newly developed zeolite material. This typical industry driven project also provides important suggestions for future industrialization of laboratory research. Key messages from this roadmap are:

1) The employment of laboratory results into industry could take decades;
2) Recovery of low concentration methane benefits environment, economy and energy;
3) Qualified natural gas products can be produced through adsorption techniques.

Image 1:

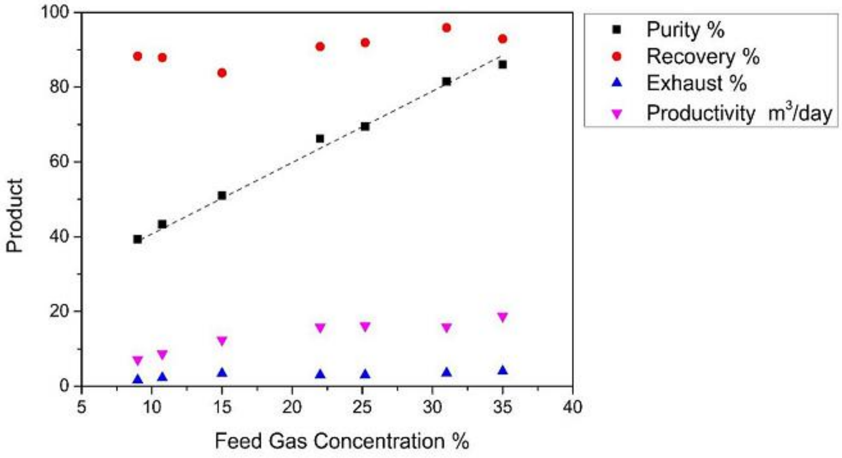

Image 2:

References: 10.1016/j.cej.2019.123753
10.1016/j.seppur.2019.116215

Industry Discussion Session
FEZA21-OR-135

New Zeolites – The Long and Winding Road from Lab to Production

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Abstract Text:

Introduction

The commercial scale production of zeolites has been established for more than 50 years. The first commercially produced zeolites were synthesized without templates. These included zeolites A, X, Y, and MFI. They were later followed by zeolites such as BEA and a high-silica MFI, which had been synthesized using templates. Further advancements in synthesis techniques allowed for the commercial production of varying modules, ion-exchangeabilities, and structures of zeolites. While, today, many commercial zeolites are produced, the need for new and experimental zeolites on a commercial scale is ever increasing. Recently, small-pore zeolite structures have become increasingly relevant as they are being used as catalysts in automotive emission control systems, as well as for the production of light olefins from methanol. Zeolite producers are now faced with new challenges related to the production of these structures. One of these is the need for new templates to be implemented in the production processes. In parallel, regulations such as REACH as well as stringent emission controls have increased globally in the last decade. These regulations require intensive preparation for bringing new structures – and with them new chemicals as raw materials and intermediates – to production plants. In literature, several novel preparation methods of zeolites with promising catalytic properties are reported, but many prove difficult, if not impossible to follow during commercial scale-up.

Experimental

Typical recipes of small-pore zeolites with AEI, CHA and LTA structures are presented. The evaluation of representative preparations with respect to their potential scale-up is shown and discussed. TG/MS and headspace GC are used to evaluate synthesis feasibility and the impact of processing with respect to the physico-chemical properties of received zeolites are presented.

Results and Discussion

The challenges in synthesis, calcination, and ion exchange of new small-pore zeolite products begin with the choice and availability of raw materials. The required templates are often not available in commercial scale and intensive safety analysis of the templates are mandatory. The chemical and technical compatibility of raw materials, products, and waste streams with existing equipment often requires significant modification and investment especially with respect to residual metal concentration in plant waste water. Often, synthesis recipes are not commercially attractive due to space-time yield and/or the subsequent treatment of the as-synthesized zeolite to achieve the final product is overly time-consuming due to the number of process steps.

Conclusions

Although there are a variety of technical and commercial obstacles, some of them can be over-come and solutions for alternatives can be found, so that new zeolite products find their way from production to market.

Industry Discussion Session

FEZA21-OR-137

Fast optimisation of MOF syntheses – bespoke, budget, in-situ monitoring to guide production

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[1]New Applications, Johnson Matthey, Reading, [2]Inorganic Chemistry Laboratory, University of Oxford, Oxford, [3]School of Chemistry, University of Birmingham, Birmingham, United Kingdom

Abstract Text: Affordable and readily available microelectronics are becoming more prevalent in teaching laboratories however these useful and economic tools are not used widely in either academia or industry research.
Herein we report how the STA-16 framework[1] synthetic routes can be optimised using an *in-situ* monitoring apparatus designed in-house on open source hardware for under $ 100.
We will demonstrate not only that the MOF can be produced at atmospheric pressure, an improvement over previous reports, but with a reduction in reaction time of 93 %. This improvement in reaction time was predicted after a single experiment using the monitoring kit showing how efficiencies in the lab can be gained with very little experimental and monetary overhead while minimising the resources used.
Additionally, system specific information can be gained, such as crystal phase identification and yield, using the same apparatus. This allows for faster research feedback loops improving efficiencies and return on research investment.
This methodology is applicable to a wide range of other MOF systems as well as other systems where a precipitation occurs, such as the production of metal oxides, zeolites and polymerisation.

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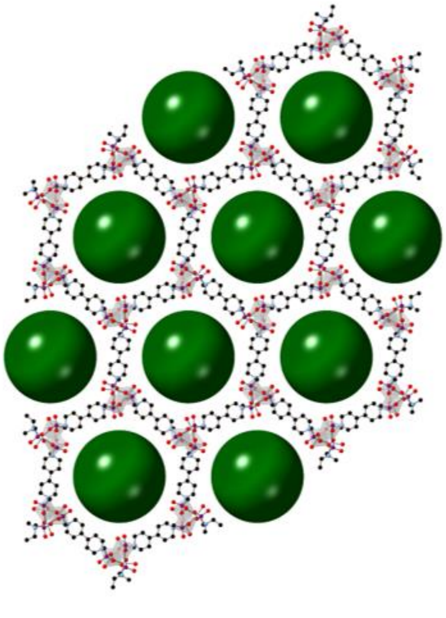

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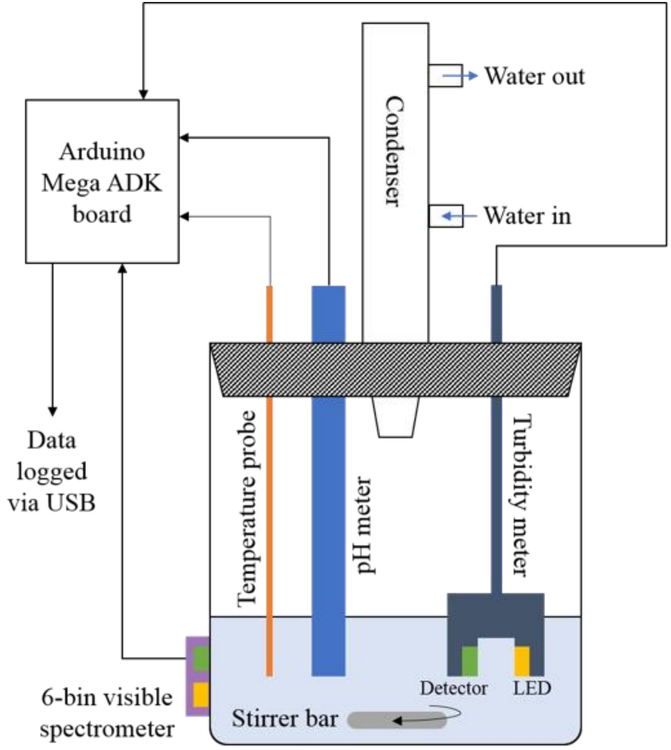

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Industry Discussion Session

FEZA21-OR-138

Developing Markets for Titanium Metal Organic Frameworks

J. Ornstein*, A. Boehme

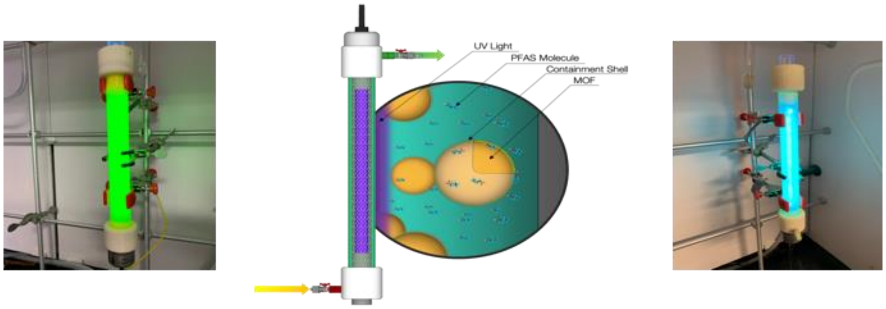
Abstract Text: Titanium Metal Organic Frameworks (MOFs) show the promise of both leveraging the photocatalytic capabilities of titanium dioxides and the stability of a tetravalent MOF[1]. framergy, Inc., of College Station Texas, is the exclusive licensee of Centre National de Recherches Sientifique's Standard Essential Patent (SEP) which governs all titanium carboxylate designs. In such, the Company needed to identify commercial applications for Ti MOFs, in consideration of their potential higher cost when compared to other MOFs. Two approaches were pursued to identify health related applications: 1) the personal care market, and 2) the water treatment field.

With the understanding that TI MOFs have can scatter UV light through their highly accessible and large surface area,[2] the framergy team formulated compositions of AYRSORB™ T125 and MIL-177HT (<1 % wt/wt) with organic sunscreen carriers squalene and oxybenzone, and tested for UV adsorption. Adsorbance was found to be consistently above 2.5 in the in the UV-C, UV-B, and UV-A spectrums. Because commercial sunscreens which use titanium dioxide can generate free radical reactive oxygen species (ROS) that can cause DNA damage,[3] tests were conducted to determine if ROS squalene byproduct peroxides could be scavenged by the MOF after UV exposure. Testing showed that squalene was reduced but no squalene monohydroperoxide isomers were detected, suggesting that MIL-125NH_2 adsorbed these organic peroxides. Further supporting data tested for any UV DNA damage, using mouse embryonic fibroblasts (MEFs) and non-tumoral fibroblast cells, was performed by Baylor University - Medical Center in Houston, Texas.

With the understanding that Ti MOFs have can catalyze organic substances through UV exposure[4] the framergy team sought to degrade per- and polyfluoroalkyl substances (PFAS) in water. Due to their environmental persistence, toxicity, and global use, PFAS remediation has gained increasing attention. The company designed and manufactured through 3D printing 100 mL reactors with a mercury light source running through the center of the reactor with the goal of developing a novel water pretreatment system. In simulated contaminated waters, both AYRSORB™ T125 and MIL-177HT showed excellent PFAS capture and degradation. Efficiencies of breaking down PFAS into more benign organics was raised from single digest to 69 percent. This is the first known example of photoactive degradation of PFAS using a MOF, and some evidence suggests that the MOF adsorbed the resultant benign organics.

framergy is at the forefront of developing markets for MOFs. Unfortunately, with new technology, the inventor is obligated to create both the technology and its application. Ti MOFs posed a greater challenge due to the higher cost of titanium inputs and the limited examples of structures in the literature[5]. In this case study, it was shown that by focusing on the critical differences of the MOF chemistry, new commercial segments could be discovered.

Image 1:



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Industry Discussion Session

FEZA21-OR-139

Zeolite Crystallization via Staged Addition of Reagents

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[1]Environmental Catalysts, BASF Corporation, Iselin, NJ, United States

Abstract Text:

Traditional zeolite synthesis relies on the batch mixing of a silica source, an alumina source, a mineralizing agent, and (possibly) an organic structure directing agent (OSDA) at the gel preparation stage. In the novel approach described herein, zeolite components are delivered during crystallization, so that the composition of the gel is not constant as function of time. The delivery of neat solutions was performed with an HPLC pump-based apparatus connected to stirred 300 ml stirred autoclaves. This approach, referred to as "delayed" or "staged" addition has been utilized to impact the quality or functionality of zeolite products; including morphology and aluminum/silicon distribution in aluminosilicate chabazite (CHA) zeolite. Furthermore, staged addition of a water-soluble aluminum source has been shown to accelerate crystallization kinetics in this system. In addition to tuning structure and composition, this methodology has yielded significant insights into mechanisms of nucleation, crystal growth, and aluminum incorporation.

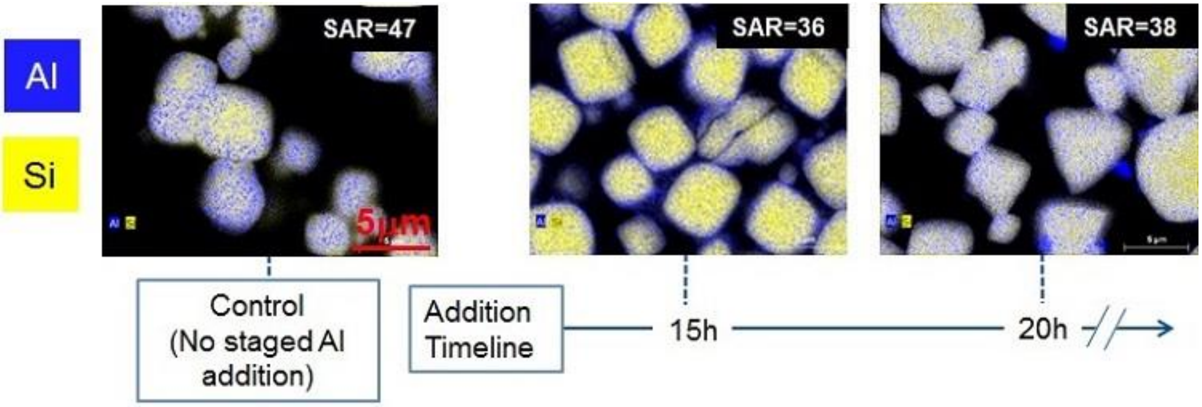
The performance of zeolite catalysts is often determined by crystal morphology and the distribution of Broensted acid sites (associated with AlO_4 tetrahedra) within the crystal. Smaller crystals are desired in applications where diffusion limitations are critical, whereas larger crystals allow for lower pressure drop. We show that the crystal size of a CHA product with silica to alumina ratio (SAR) of 24 is dependent on the time of addition of sodium aluminate solution to a SAR=32 gel. Smaller crystals (200-500 nm) form when sodium aluminate is added during the nucleation stage, whereas larger crystals form if this Al source is introduced at a later crystallization stage or during gel makeup.

The synergy of minimal diffusion limitations and desirable flow characteristics may be achieved in a large crystal material with a surface enrichment of active sites (surface aluminum enrichment). Although zeolites with compositional gradients have been observed to form in traditional batch zeolite synthesis [1], due to a variation in rates of silicon and aluminum dissolution/ incorporation, there is currently no method of actively controlling this distribution. By adding controlled amounts of sodium aluminate during crystal growth, we have demonstrated the formation of 3-5 micron SAR=36 CHA crystals with an aluminum rich outer shell. Addition of this secondary aluminum source prior to crystallization, or at late crystallization stages, results in the formation of a product with a uniform aluminum distribution or a segregated alumina phase, respectively. The spatial aluminum distributions were studied by scanning electron microscopy (SEM) with energy-dispersive X-ray (EDX) elemental mapping (Figure 1), and X-ray photoelectron spectroscopy (XPS) with continuous argon sputtering.

Liu *et* al. [2] have shown that soluble aluminum species can inhibit CHA crystallization, and that using aluminum sources with a low solubility results in a low steady state soluble aluminum concertation, thus leading to faster crystallization. This approach is simulated herein by introducing a soluble aluminum source continuously during CHA crystallization. The result is a fully crystalline product in one-third of the time required for standard batch crystallization. Cu-CHA catalyst prepared with the aforementioned product shows similar SCR performance to Cu-CHA prepared via batch crystallization.

Figure 1. Schematic representation of sodium aluminate addition to SAR=56 CHA gel during crystallization. Each point on the time-line represents the addition of sodium aluminate solution at the indicated time and an elemental map of the corresponding product crystals after 30h crystallization.

Image 1:



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Physical Properties and the Role of Defects

FEZA21-OR-140

OPERANDO MODELLING OF ZEOLITE HYDROLYSIS: SOLVATION, DEFECTS AND pH EFFECTS

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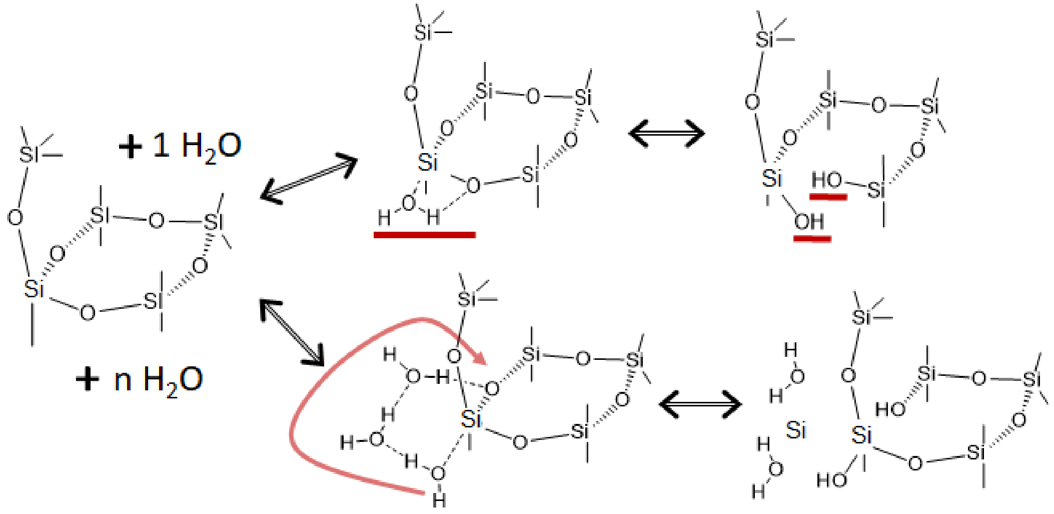
Abstract Text: .Zeolites are commonly found and frequently used under hydrated conditions, ranging from high temperature steaming conditions, under low water partial pressures, to full water solvation at room temperature for biomass catalysis applications. Under all such regimes, it is crucial to understand the factors which control stability and reactivity, including water loading, defects and pH. However, the dual nature of water as both a solvent and a reactant, and the complexity of the system under *operando* conditions makes this an ongoing challenge.[1]

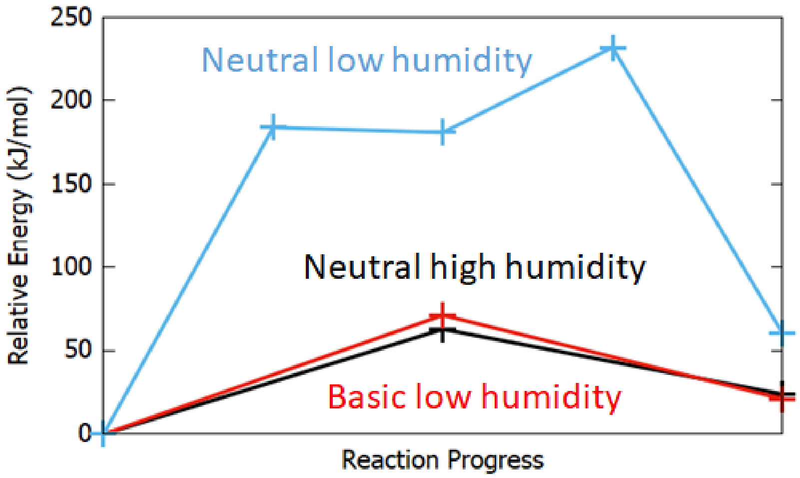
We have recently shown, by way of *ab initio* molecular dynamical simulations, that the degree of solvation greatly impacts the reactivity and stability of both purely silicious and aluminosilicate zeolites.[2,3] Even under mild, neutral conditions, increasing the water loading enhances the thermodynamic stability of hydrolysis products and changes the preferential reaction mechanism, lowering reaction barriers and leading to remarkable room temperature framework lability in CHA.[3] In the current work, we identity and quantify the role of solvation in hydrolysis under acidic and basic conditions. Water loading is again found to play a complex and multi-faceted role. Cooperativity of water molecules is found to help pre-organise the reactant (HCl/NaOH) towards attack at the framework. Water cooperativity also induces the catalytic regeneration of the acid/base for subsequent reaction steps.

Our findings isolate and numerate the subtle effects which control hydrolysis under realistic conditions. In particular, they highlight the necessity of an *operando* description of the interior of the zeolite pore, with a particular focus on water.

Figure 1. Above: Mechanism of neutral water hydrolysis under low and high humidity for Si-CHA. Below: DFT energetics of hydrolysis (1st step), including basic conditions.

Image 1:





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Physical Properties and the Role of Defects

FEZA21-OR-141

Weak CH…O hydrogen bonds in as-synthesized zeolites: investigation of a widespread and often neglected intermolecular interaction

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[1]CNRS - ICGM, ICGM, Montpellier Cedex 5, [2]LCS, ENSICAEN-CNRS-U.Normandy, Caen, [3]L2C, UM-CNRS, Montpellier, France

Abstract Text:

Weak hydrogen bonds (HBs) between CH donor groups and O acceptor atoms have been evidenced and described for several biological molecules, and have a recognized role in organic and organometallic chemistry.[1] In the case of oxide-based materials like zeolites, the implication of these HBs in crystal formation is scarcely investigated.

Weak CH…O HBs are not easily identified as their individual signature can be very subtle, and often blurred in the ensemble of intermolecular interactions. In the case of Organic Structure Directing Agent (OSDA)-zeolite framework interactions, the difficulty is enhanced by the static and thermal disorders at the crystallographic positions. Moreover, the large number of unequivalent atoms in zeolites with complex topologies still hinders the identification of CH…O HBs. Despite these difficulties, considering these HBs when discussing OSDA-zeolite interactions would be beneficial for the design of the final zeolite structure and properties.

Tetraalkylammonium cations, widely used as OSDAs in the synthesis of zeolites, are known for a long time to form CH…X HBs with proton acceptor anions.[2] Besides, Behrens *et al*. showed the presence of HBs between the aromatic CH groups of the organometallic cobaltocenium cation $[Co(C_5H_5)_2]^+$ and the O atoms of silica in the particular case of the clathrasil NON framework.[3] Recently, we studied the possible role of intermolecular CH…O HBs inside the clathrasil AST obtained through a fluoride route.[4] The measured ^{14}N NMR quadrupolar coupling constant is higher than that expected for a freely reorienting TMA$^+$. It can be explained by a structural model obtained through DFT calculations. In addition to Coulomb and Van der Waals interactions, the analysis of this model highlights the presence of other interactions - Si-F tetrel bondings inside D4R cages, CH…O HBs between TMA$^+$ and O in framework - that contribute to the whole stabilization of the OSDA-zeolite assembly.

For a more complex topology like MFI, a first evidence of the presence of CH…O bonds comes through the analysis of the crystal structure of as-synthesized silicalite-1 containing tetrapropylammonium (TPA$^+$) and F atoms. Several C…O distances are below 3.6 Å and can be related to the presence of weak HBs. A second experimental indication of CH…O HBs is obtained from IR measurements as a function of the temperature. Two small but significant gradual downshifts for ν(CH) localized at ~2850 ($\Delta\nu_{(275\text{-}180K)}$ = 4cm^{-1}) and ~2917 cm^{-1} ($\Delta\nu_{(275\text{-}180K)}$ = 2cm^{-1}) can be explained by at least one type of CH$_x$ groups involved in HBs. A dynamics simulation of a cluster model centered on TPA$^+$ (at T = 300 K for 1.1 ps) was highly compatible with the experimental crystallographic and ^{13}C and ^{14}N NMR data. It allowed to evidence 28 weak CH…O HBs that represent 30% of the energy of the Coulomb electrostatic interaction between OSDA and the zeolite framework. The strongest and most stable HB found here connects the OSDA to the $[4^15^26^2]$ cage containing F atoms and should contribute to preserve zeolite topology during crystal growth (Figure).[5]

A more recent investigation of a series of OSDA-zeolites assemblies (crystal structures and DFT optimized models) with very different framework topology confirms the widespread presence of directional CH...O HBs.[6] These HBs are therefore important host-guest interactions in zeolite chemistry that will have to be considered when discussing zeolite structure directing phenomena.

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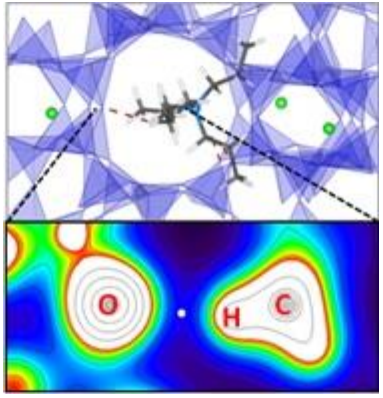
Image 1:



Physical Properties and the Role of Defects

FEZA21-OR-142

DFT-based molecular dynamics elucidate the dynamic behaviour of fluoride anions in all-silica zeolites

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Abstract Text: Introduction

The “fluoride route”, synthesis in the presence of fluoride anions, is a versatile strategy to obtain high-quality crystals of all-silica zeolites. Furthermore, it has led to the discovery of several new zeolite frameworks that are not synthetically accessible in the absence of fluoride.[1,2] The fluoride anions are incorporated into the zeolite structure, occupying small cages and balancing the charge of the cationic organic structure-directing agents (OSDAs) that fill the larger cages or channels. Diffraction investigations on as-synthesised zeolites have shown that fluoride anions often form covalent bonds to framework Si atoms, e.g., in Silicalite-1 (MFI framework type),[3] in ITQ-4 (IFR),[4] and in all-silica chabazite (CHA).[5] In many systems, fluoride anions are disordered over two or more positions, and solid-state NMR experiments permit a distinction between dynamic and static disorder.[6] However, neither diffraction nor NMR methods are able to fully elucidate the reasons for the varying degree of dynamic disorder observed among different zeolite frameworks.[4] In this contribution, ab-initio molecular dynamics (AIMD) simulations based on dispersion-corrected density functional theory (DFT) are employed to obtain atomic-level insights into the dynamic behaviour of fluoride anions, especially regarding the influence of the local structural environment.

Comparison of different zeolite frameworks

In previous work on Silicalite-1, dynamic “events”, i.e., movements of a fluoride anion from one Si atom to a neighbouring one, occurred during the AIMD simulations.[7] These events are detectable as discontinuous changes in the atomic coordinates (see Image 1). AIMD simulations of five different all-silica zeolites reproduce the qualitative differences in the dynamic behaviour of fluoride anions, in agreement with previous NMR results. Even the rather complex dynamic disorder of fluoride over three non-equivalent sites in STT-type SSZ-23 is observed in the AIMD trajectories.[8] An in-depth analysis of the local environment of fluoride in the different zeolites reveals that the proximity of next-nearest neighbouring silicon atoms plays a key role in determining whether dynamic disorder occurs or not. Furthermore, attractive interactions with the OSDA can suppress the dynamic behaviour in certain cases.

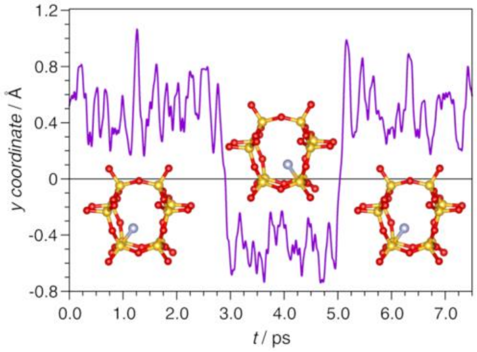
ITQ-13, a zeolite with fluoride in different environments

The zeolite ITQ-13 (ITH framework) is an unusual case as the fluoride anions occupy two different environments in the crystal structure of the as-synthesised form.[9] While the anions occupying the centre of double four-ring cages cannot be removed upon alkaline treatment, those that are covalently bonded to single Si atoms are more easily removed.[10] Using an AIMD-based approach, the dynamics of fluoride anions in these different environments are compared. In addition to studying the pure-SiO2 end member, different silicogermanate compositions are considered to assess the effect of germanium incorporation on the relative stability of the two fluoride positions and on the dynamic behaviour.

Image 1: Evolution of the coordinate of one fluoride anion during an MD trajectory. The two discontinuities at ~3 and ~5 ps correspond to dynamic events.

Funding by the DFG (project number 389577027) is gratefully acknowledged.

Image 1:



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Physical Properties and the Role of Defects

FEZA21-OR-143

Energetics and Structure of Ag-Water Clusters Formed in Mordenite

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Abstract Text: Zeolite supported Ag^0 clusters exhibit broad applications including gas separation, catalysis, and biomedical applications, necessitating a mechanistic understanding of the *in situ* formation of Ag^0 clusters. Density Functional Theory (DFT) simulations have been performed on silver, water, and silver-water clusters in mordenite to identify the impact of confinement on the structure and energetics of Ag^0 cluster formation. The most stable cluster in the 12-membered ring (MR) pore of mordenite is a 10-15 atom Ag^0 cluster, and hydrated Ag^0 clusters are consistently less energetically favorable. Computational pair distribution function (PDF) data indicated that structural differences between the Ag^0 and Ag^0-H_2O clusters formed in vacuum versus in mordenite, including lower densities and higher surfaces areas for confined clusters, hypothesized to be due to the limiting geometry of the 12-MR main channel. The formation of larger Ag^0 clusters was also identified as energetically favorable, with fully hydrated silver atoms generating higher energy structures. Overall, this work demonstrates a drive towards formation of Ag^0 clusters and identifies mechanistic and structural insight into the role of nanoconfinement on formation of Ag^0 clusters in mordenite. Sandia National Laboratories is managed and operated by NTESS under DOE NNSA contract DE-NA0003525. SAND2020-0414 A.

Physical Properties and the Role of Defects

FEZA21-OR-144

Dynamics of a flexible GIS framework tuned by Al-distribution and cation-guest interaction

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Abstract Text: High-silica gismondine with a Si/Al ratio of three has been discovered to show exceptional CO_2 ad- and de-sorption properties which go along with a surprisingly strong and fully reversible framework deformation. NMR-crystallography, a combination of powder X-ray diffraction and solid-state nuclear magnetic resonance, has revealed that this exceptional performance his caused by a subtle interplay between framework-oxygen and CO_2 molecules, competing for complexation of the extra-framework cations. The resulting, tuneable framework deformation, is controlling the available pore space and can be exploited for adjusting the temperature requirements for efficient temperature swing processing at mild conditions.

The discovery how the physicochemical properties of extra-framework cations govern reversible changes of available pore space may very well initiate a paradigm shift in how zeolites are used in sustainable processing, including CO_2 control.

This contribution will show in detail how the structural details in this complex system became accessible using ^{29} Si, ^{27} Al, ^{23} Na, and ^{87} Rb NMR in combination with modelling and structure solution from powder X-ray patterns.

The figures show, the solved structures for Na-GIS and Rb-GIS in function of guest molecule (image1) and the corresponding X-ray and ^{29}Si-NMR data next to the deformations of the 8-ring channels (Image 2; top row Na-GIS, bottom row Rb-GIS)

Image 1:

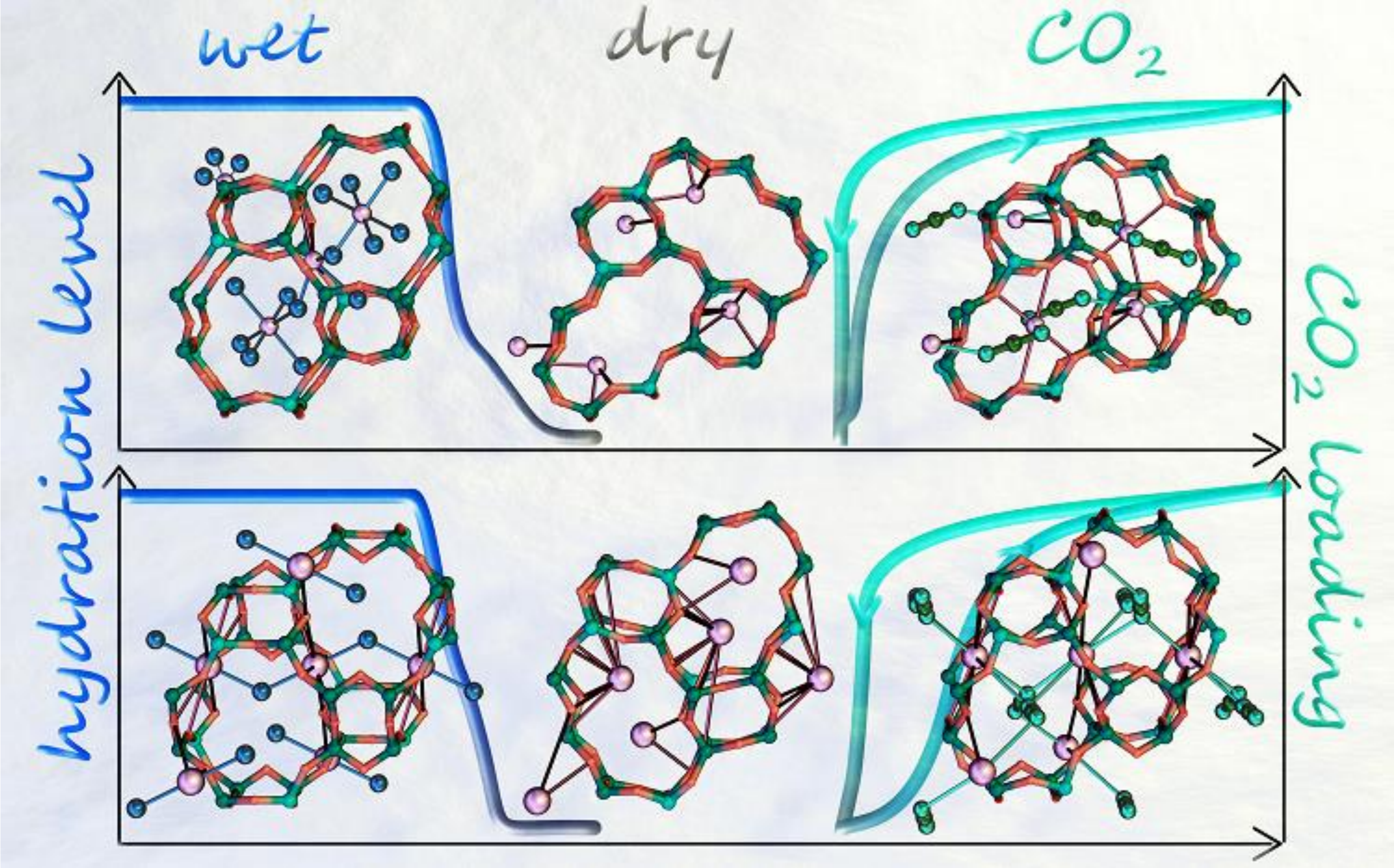
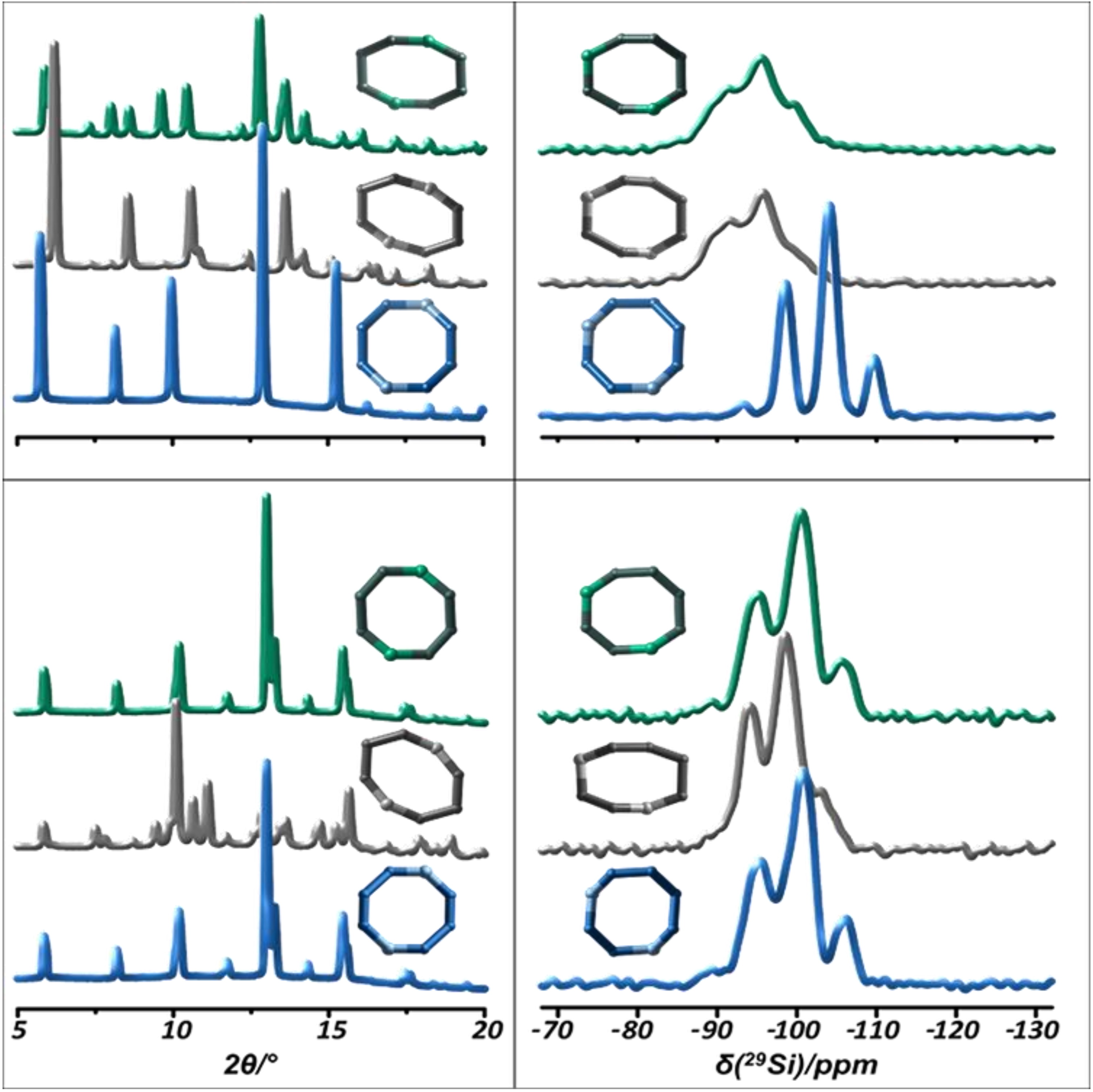


Image 2:



Physical Properties and the Role of Defects

FEZA21-OR-145

CrystalGrower: Modelling the Crystallisation of Porous Materials

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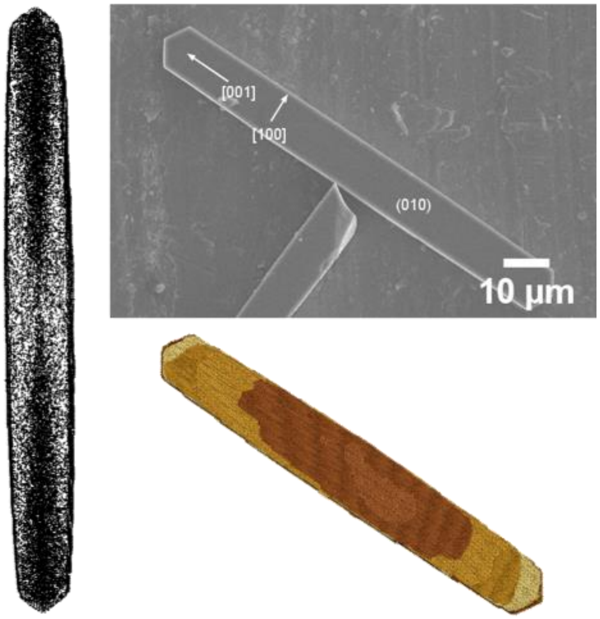
Abstract Text: In the synthesis of crystalline materials, small changes to reaction conditions can have dramatic impacts on crystal morphology, crystal size and the density of defects. For porous materials, changes to crystal shape impact pore length and accessibility, whilst defects can disrupt porosity. This can impact mass transfer properties, and thereby greatly alter suitability of materials for applications as catalysts or absorbents. On these grounds, there is significant incentive to improve understanding of how reaction conditions link to crystal morphologies, and for development of methods to model crystallisation and dissolution processes.

With these aims in mind, this work uses the software *CrystalGrower* to model the crystallisation and dissolution of porous materials,[1] focussing on the examples of offretite, silicalite and $AlPO_4$-5. *CrystalGrower* uses kinetic Monte Carlo simulations to model crystallisation, with each Monte Carlo trial representing a growth or dissolution event. Through an interface with the software *ToposPro*,[2] structures are partitioned by a natural tiling approach,[3] with the resulting tiles used as building blocks in kinetic Monte Carlo simulations of crystal growth. Probabilities for growth and dissolution events are calculated from energy changes for attachment and detachment. An estimate for these energy changes can be obtained through fitting simulations to experimental data. Such experimental data includes that obtained through scanning electron microscopy and atomic force microscopy (AFM). AFM data reveals terrace structures in each example material, along with evidence of growth at screw dislocations in offretite and silicalite. Use of *CrystalGrower* is shown to predict an inhomogeneous distribution of defects in both silicalite and $AlPO_4$-5, which shows a striking resemblance to previously reported hourglass patterning in the optical properties of these materials.[1,4]

Image 1: Left – Inhomogeneous distribution of defects, predicted by CrystalGrower to be present in silicalite crystals. Right - Scanning electron micrographs of silicalite crystals, alongside representation of simulated crystals generated using CrystalGrower.

Image 1:



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Physical Properties and the Role of Defects

FEZA21-OR-146

Luminescent Properties of DOBDC MOFs: the Role of Free Hydroxyls

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Abstract Text: A novel metal-organic framework (MOF), Mn-DOBDC, has been synthesized to investigate the impact of the metal center (transition metal vs lanthanide) and free linker hydroxyls on the luminescent properties of DOBDC (2,5-dihydroxyterephthalic acid) containing MOFs. Mn-DOBDC contains similarities shared between M-MOF-74 and RE-DOBDC, including a 2+ transition metal similar to MOF-74, and non-covalently bound hydroxyls on the DOBDC linker, similar to reported RE-DOBDC MOFs.

In this work, M-MOF-74 (M – Co, Mg, Ni, Zn), RE-DOBDC (RE – Eu, Tb, Y, Yb) and Mn-DOBDC were synthesized and analyzed by powder X-ray diffraction (PXRD) and the fluorescent properties probed by UV-Vis spectroscopy and density functional theory (DFT). Mn-DOBDC synthesis used a concurrent facile reflux synthesis and slow crystallization to afford yellow single crystals in monoclinic space group C 1 2/c 1. Further analysis of Mn-DOBDC by single crystal X-ray diffraction (SCXRD) and scanning electron microscopy – energy dispersive spectroscopy (SEM-EDS) was performed to collect unit cell data and confirm uniform morphology, respectively. Mn-DOBDC retained the luminescent properties of the DOBDC linker which occurs in RE-DOBDC, due to the free hydroxyls on the linker, as seen in computational DFT results. In MOF-74 however, the luminescence is quenched due to binding of the phenolic hydroxyls within the MOF structure. Therefore, the free hydroxyls, and not the metal center, control the majority of the luminescence in DOBDC MOFs.

* This work was supported as part of UNCAGE-ME, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award #DE-SC0012577. SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525

Physical Properties and the Role of Defects

FEZA21-OR-147

Nanoconfinement of water and an ionic liquid solution in mesoporous host materials

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Abstract Text: The confinement of liquids in porous media greatly influences their physical properties, in particular, when the pore size approaches the molecular length scale. Several mechanisms, such as the pure geometrical restriction and the liquid-solid interaction at the interface contribute to the confinement effects, however, their roles for the drastic changes in the thermal and dynamic behaviors of the liquids are not clearly understood.

Here we present the results of two studies dealing with the behavior of a confined liquid and solution in different host materials: a) water in periodic mesoporous organosilicas (PMOs) with different chemical organic bridging units and pore sizes in the range of 2-5 nm and b) ionic liquid (IL)-based electrolytic solution (Li^+TFSI^- in $Pyr13^+TFSI^-$) in nanoporous (RF) polymer monoliths with 3d pore structure and pore sizes ranging from ca. 7 to 60 nm.

Nanoconfined water in PMOs

In contrast to the pristine silica the periodic mesoporous organosilicas can contain organic bridging units within the quasi-crystalline pore walls and therefore a periodically modulated surface polarity [1]. To study the thermodynamic properties of water in these confined spaces melting and freezing points were measured by DSC and T dependent ^1H solid state MAS NMR. The m.p. of water in different PMOs is shifted by approximately 5-10 °C compared to the pristine silicas with the same pore diameter. This is probably due to the different adsorption and pore filling phenomena of water in these materials with localized more hydrophobic and therefore water repelling structural units. To obtain information about the localization of water in PMOs 1D and 2D HETCOR NMR (^{29}Si-/^{13}C-^1H) solid state MAS NMR measurements were carried out. It could be shown that the water is much closer localized to the inorganic regions of the pore wall than to the organic because of the different surface polarities and the non-wetting properties [3]. Finally water transport was studied using pulsed field gradient (PFG) NMR spectroscopy [4].

IL solution in mesoporous RF monoliths

Thermal analysis of RF polymer/ionic liquid composites showed stability up to almost 400 °C and a melting point depression proportional to the inverse of the pore diameter. Good ionic conductivity comparable to that of a commercial separator is obtained, which is dependent on the porosity (i.e., pore volume) of the confining host material (i.e., the number of charge carriers available in the system). Further PFG NMR experiments revealed that the diffusion coefficient of $Pyr13^+$ cation becomes smaller than that of $TFSI^-$ anion inside RF pores, which is contradictory to the bulk IL system. This change in the ionic motion is due to electrostatic attraction between the pore walls and $Pyr13^+$ cations, resulting in a layer structure composed of a $Pyr13^+$ cation-rich layer adsorbed at the pore wall surface and a $TFSI^-$ anion-enriched bulk-like layer at the pore center. Our study suggests that transport characteristics of the ions of interest can be controlled by optimizing the surface chemistry of the host framework and their motion can be separately monitored by PFG NMR spectroscopy [4].

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Physical Properties and the Role of Defects

FEZA21-OR-148

Dynamics and Reactivity of Methanol in zeolite H-ZSM-5

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Abstract Text: Catalytic processes as used in the petrochemical industry for production of transportation fuels and vehicle exhaust after-treatment play a significant role in our social, environmental and economic spheres [1,2]. In a catalytic process involving gas-solid system, transportation of reactants from the gas phase to the porous catalyst surface and then to the active site located within the catalyst pores with distinct pore architecture involves adsorption, diffusion and reaction of reactant molecules at the active site. After the reaction, the products desorb and diffuse through the catalyst pores back in to the gas-phase product stream. Therefore, diffusion is one of the key components of a catalytic process that needs to be quantified in order to develop efficient processes. In this regard, the knowledge of adsorption geometry and reactivity of diffusing molecules at the active site of catalyst pores can complement our understanding of the diffusion mechanism. Here we report methanol dynamics and reactivity in zeolite H-ZSM-5 pores in the context of methanol to hydrocarbons (MTH [3,4]) process, which is one of the key petrochemical processes for transportation fuels (methanol to gasoline, MTG) and polymer grade olefins (methanol to olefins, MTO [4,5]), by quasi-elastic neutron scattering (QENS) and infrared spectroscopy (IR). To this end, zeolites H-ZSM-5 with different Si/Al ratios were studied by QENS and IR. QENS data show, within the instrumental resolution, that methanol mobility is restricted, though to different degrees depending on the temperature and Si/Al ratio of H-ZSM-5 [6,7], which is attributed to the hydrogen bonded methanol and methoxylation as evident from IR spectroscopy [8,9]. The effect of Si/Al ratio of H-ZSM-5 on the nature of methanol dynamics and reactivity in the zeolite pores will be discussed.

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Stimuli Responsive Behaviour and Emerging Properties

FEZA21-OR-149

A CuO@KIT-6 Silica Nanocomposite for Highly Selective H2S Gas Sensing

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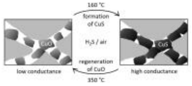
Abstract Text: A host-guest composite material of copper(II) oxide nanoparticles (CuO) dispersed in mesoporous KIT-6 silica (SiO_2) is used as a dosimetric sensor for hydrogen sulphide gas (H_2S) in low ppm concentration. The sensor principle is based on the reversible chemical conversion of CuO to CuS, which guarantees a high selectivity, and on the corresponding percolation-induced change in electronic conductance.

CuO is a promising material for the dosimetric detection of H_2S gas in low ppm concentrations.[1] When exposed to H_2S at moderately elevated temperature (160 °C), it will react to form copper(II) sulphide: $CuO + H_2S \rightarrow CuS + H_2O$. Since CuS is highly conductive ('metallic' CuS), the reaction results in a strong increase of electronic conductivity. The conversion is reversible; CuO is regenerated by heating to 350 °C in air ($2\ CuS + 3\ O_2 \rightarrow 2\ CuO + 2\ SO_2$; with or without H_2S present). The sensor principle is based on monitoring the conductivity of the material during repeated cycles of CuS formation and CuO regeneration.

We present a composite material of CuO nanoparticles prepared *in situ* inside the pores of mesoporous KIT-6 silica[2] by wet impregnation. The material is used as a dosimeter-type H_2S sensor. Long-term stability of our system allows for repeated cycles of measurement and regeneration.[3] This is possible owing to the fact that the CuO/CuS nanoparticles are embedded in the nanoporous matrix. Even though severe volume expansion and shrinkage of the particles take place during each cycle, no overall morphological changes in the sensing material occur, which ensures a stable long-term sensing performance. The sensor response is marked by a percolation-type mechanism.[4] Upon exposure to H_2S the conductance remains low for a certain induction time during which CuS is gradually formed. Once the percolation threshold is reached, a continuous conduction path forms and the conductance shows a steep increase. The length of the induction period depends on the H_2S concentration; hence, measuring this time period allows for assessment of the H_2S concentration (after calibration).

Image 1:



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Stimuli Responsive Behaviour and Emerging Properties

FEZA21-OR-150

Revisiting Water Sorption Isotherm of Porous Solids Using Electrical Measurements

S. Nandi [1], H. Aggarwal [2], M. Wahiduzzaman [1], Y. Belmabkhout [2], G. Maurin [1], M. Eddaoudi [2], S. Devautour-Vinot [1,*]
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Abstract Text: Octamethylcyclotetrasiloxane (commonly named D4) is one of the most representative Volatile methylsiloxanes (VMS) contaminants in biogas streams [1]. Conventional adsorbents such as activated carbons, silicas, and zeolites have been considered for D4 capture [2], however so far they have not reached the three key criteria together, i.e. high uptake, good selectivity vs. water, and easy regeneration. MOFs appear as promising alternative adsorbents due to their highly porous structures, and tailorable chemical and physical properties, but only a very few studies have envisaged their uses for the adsorption of this target molecule. [3, 4] Herein, high-throughput molecular simulations were performed to screen the recent Computation-Ready Experimental (CoRE) MOF database for D4 capture. We selected the hydrophobic MOFs whose pore limiting diameters larger than 6.0 � to accommodate this relatively bulky molecule. A Zr-MOF was identified as a good candidate in terms of D4 uptake and affinity and this guided the experimental effort towards the synthesis of this sample and adsorption testing. [5] This mesoporous MOF was demonstrated to have a record D4 uptake of 1.8 g g-1 which is almost twice higher than the performance of the benchmark MIL-101(Cr). Remarkably, this MOF shows an exceptional cyclability combined with an easy regeneration. We further investigated the adsorption mechanism at the origin of this spectacular performance. This hybrid computational-experimental approach will guide further development of MOFs for the capture of other molecules of this family of VMS.

Image 1:

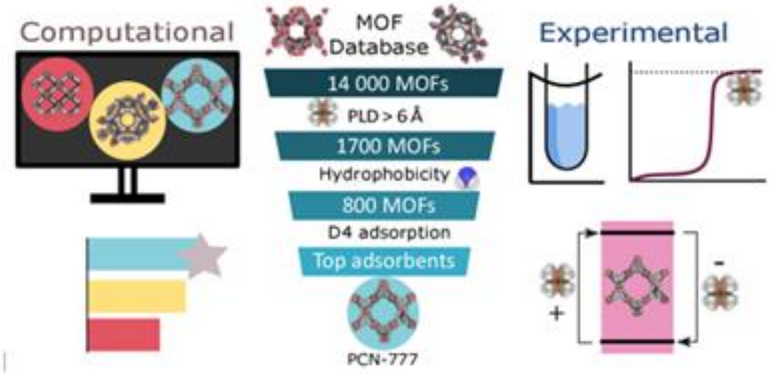

Figure: *schema of screening methodology, combining both computational and experimental approaches to narrow down materials for siloxane sorption.*

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Stimuli Responsive Behaviour and Emerging Properties

FEZA21-OR-151

Direct Electrical Detection of Target Environmental Gases by a Zeolite and MOF Based Sensors

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Abstract Text: Herein, we present durable direct electrical readout sensors for gas detection under ambient conditions. Detection of specific gas molecules in both industrial and environmental applications is vital for the safe operation of processes, the detection of potentially harmful gases and the protection of the environment. The development of sensors with high specificity in the presence of competing gases benefits from the incorporation of tuned nanoporous materials. Furthermore, the need for durability under a wide variety of conditions makes the use of zeolites or MOFs the ideal media for incorporation into a sensing device.

There exist a wide variety of sensing devices for gaseous molecules. The most common methodologies include (1) solid state oxide-based (SSO) devices, and (2) fuel cell (FC) type devices. Both are proven technologies. However, both have important drawbacks when considering their use in gas detection under ambient conditions. For SSO devices, high temperature operating ranges require heating devices to maintain above 200 °C for operations. For FC devices, though operational at ambient conditions, their durability is a liability due to fouling. Therefore, we are pursuing the development of a fully solid-state, direct electrical readout device. It will need to be operational with a range of different gases, have ease of readout, be inexpensive in nature and high in reliability.

Herein, we show the use of a variety of zeolite and MOF composite sensors for the targeting of important environmental acid gas and/or nuclear accident fission gases in the presence of competing air gases, under ambient conditions. The ability to successfully develop selective sensors with a variety of nanoporous materials shows the flexibility in design of the sensor concept for a variety of applications. Thin film coatings were applied to Pt interdigitated electrodes (IEDs). This design is based on our earlier successful use of both zeolites and metal organic frameworks (MOFs) for iodine detection. The resultant impedance spectroscopy (IS) properties from the sensor are described with respect to correlations between occluded ion, gas adsorption mechanisms, and charge transfer pathways from gas to nanoporous framework to sensor signal. An equivalent circuit model is developed to describe the movement of charge along the surface and through the pores of the framework.

While these previous sensors described are 'yes/no' sensors in so much as they give high fidelity to the presence of the targeted gas molecule, the ability to reuse (or multiple use) sensors is of importance to industrial applications. Therefore we will also discuss the use of nanoporous (MOFs) materials which release the gas molecules targeted with the addition of mild heat. We have successfully employed this method to a variety of sensors. Details of their performance will also be discussed.

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Catalytic Properties|Zeolites/Inorganic materials|Poster
FEZA21-OR-152

Reaction mechanism and effect of zeolite framework structure for CO-assisted methane conversion into C1/C2 oxygenates over supported Rh catalyst

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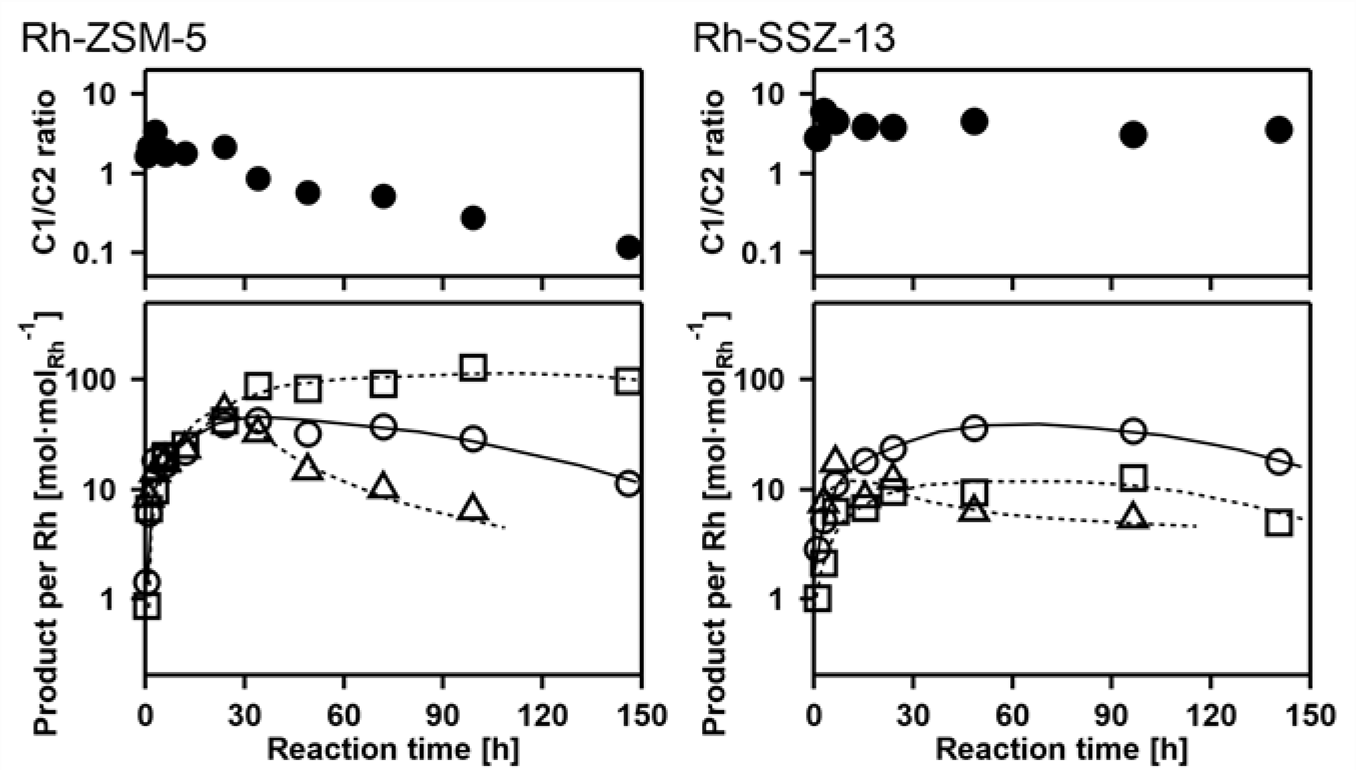
Abstract Text: Oxidative upgrading of methane into valuable chemicals, especially with using gaseous oxygen as an oxidant, has been a challenge for a long time. Since the shale gas revolution, the research field has become more active trying to find a new catalyst and establish an effective process. Cu and Fe ion-exchanged zeolite catalysts have been studied as potential candidates since early 2000s, which can produce methanol in high selectivity with using gaseous oxygen as an oxidant. On the other hand, the conversion of methene into small oxygenates including formaldehyde and acetic acid besides methanol has been demonstrated under the presence of carbon monoxide as an additive.[1-2] Since the pioneering works using Rh-ZSM-5 as a catalyst, several experimental and theoretical studies have addressed the methane oxidation reaction.[3-6]

In the present report, it has been revealed that the key factors for CO-assisted methane conversion over zeolite-supported single-atom Rh catalyst were investigated experimentally. In this system, CO and O_2 were found to act as an indispensable additive and the true oxidant, respectively. Sequential addition of the reactants suggested the formation of active oxygen-based species from CO and O_2, that subsequently react with CH_4, while CH_4 was not activated in the presence of CO alone. The critical effect of acid sites in the formation of the C2 product (i.e., CH_3COOH) was confirmed by changing the Si/Al ratio of the zeolite. However, their role was found to be limited to the formation of CH_3COOH and not methane activation itself. Based on our experimental results and previous discussions, a plausible reaction mechanism for oxygenates formation was proposed. Finally, the effect of zeolite framework was studied, and small-pore zeolite (SSZ-13) were found to be superior for the selective production of C1 oxygenates than the conventional ZSM-5 (Figure 1), most likely because the size of the pore window limits the formation of large products.

Figure 1. Changes of the amount of oxygenates formed along with reaction time over Rh-ZSM-5 and Rh-SSZ-13 catalysts, and the C1/C2 ratios (top) (0.2 MPa O2, 0.5 MPa CO, 2.0 MPa CH4, 40 mg catalyst, 8 mL water, 423 K). In the bottom graph, circles, triangles, and squares represent methanol, formic acid, and acetic acid, respectively.

Image 1:



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Biomedical Applications|Zeolites/Inorganic materials

FEZA21-OR-153

The intracellular fate of metal organic frameworks and maghemite nano-objects and the application for inflammatory diseases theranostics

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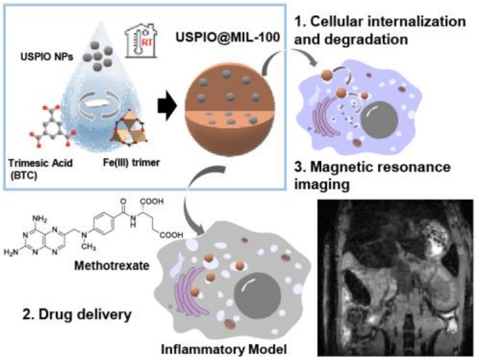
Abstract Text:

Inflammation is an essential immune response to harmful stimuli, but the inflammatory process becomes detrimental in some conditions. Anti-inflammation is a highly promising strategy for the prevention and treatment of acute and chronic inflammatory diseases. To circumvent disadvantages of anti-inflammatory therapies based on traditional formulations, different advanced drug delivery systems have been investigated over the past decades. However, most drug delivery carriers reported so far suffer from poor drug loading, non-specific delivery of drug, difficulty of by-passing physiological barriers, lack of reproducible scale-up processes, etc (1). Metal–organic frameworks (MOFs), an emerging class of hybrid porous materials based on inorganic building units and organic linkers, have shown promise in drug delivery in recent years (2). To perform parallel diagnosis/imaging and therapy tasks (“theranostics”), a wide range of nanovectors have been developed through integrating multiple components into a single nano-object, allowing monitoring the treatment in real time (3). Herein, hybrid nano-objects of MOFs and maghemite were designed for stimuli-responsive anti-inflammation and the intracellular fate of nano-objects in vitro was investigated.

The present communication deals with the design of surface-decorated or core-shell nano-objects by assembling nanoparticles of iron based MOF nanoparticles. After the loading of anti-inflammatory drug, stimuli-responsive therapeutic study was performed based on inflammation cell model. Not only are the bimodal nanovectors produced through a cost-effective and reliable green approach, but they also exhibit excellent colloidal stability under simulated physiological conditions, and their ability to encapsulate and progressively release drugs is preserved. More importantly, they combine low toxicity with high anti-inflammation activity and can be used in vivo as an efficient MRI contrast agent because of their excellent relaxivity properties. All these properties make these nano-objects bimodal therapeutic nanovectors coupling drug-delivery and MRI properties.

Image 1:



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Gas Adsorption, Separation and Storage

FEZA21-OR-155

CHA zeolite nanocrystals free of organic templates for selective CO2 capture

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Abstract Text: There is an increasing demand for porous materials able to separate the components of natural gas, mainly CH_4 and CO_2. Flexible small-pore zeolites such as nanosized chabazite (CHA) are excellent candidates for the selective separation of CO_2. However, the current synthesis of nanosized zeolites involves several steps and the use of organic structure directing agent (OSDA).$^{(1,2)}$

Here we report the synthesis of small-pore zeolite crystals (aluminosilicate) with CHA-type framework structure by direct synthesis in a colloidal suspension containing a mixture of inorganic cations only (Na+, K+ and Cs+). The CHA nanocrystals containing three extra frameworks cations have a Si/Al ratio of 2.1 (**Figure 1a** *: TEM image of the CHA zeolite nanocrystals (scale bar of 200nm)*).

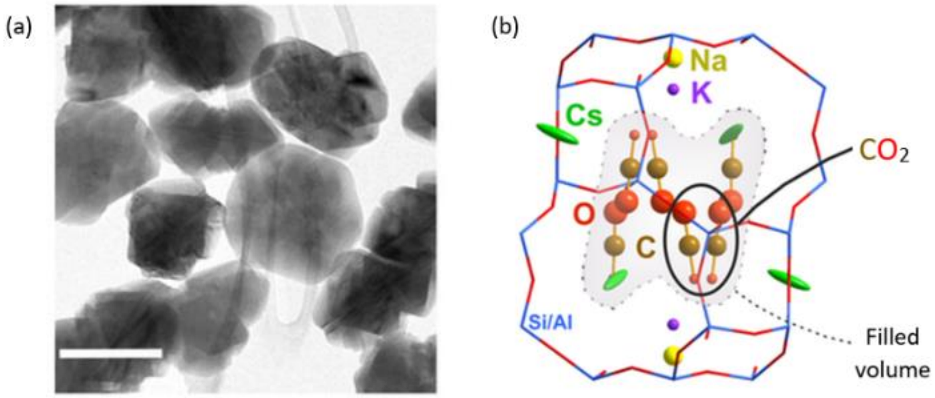
This selectivity of the CHA nanosized zeolite comes from the narrow pore sizes and shapes which can be control by the introduction of different extra-framework cations such as K^+, Na^+, Cs^+. Indeed, the extra-framework cations selectively block the access of molecules to the pores and cages of the zeolite, depending on the nature of the adsorbates.

The high sorption capacity for CO_2 (3.8 mmol/g at 121 kPa), structural stability and regenerability of the CHA zeolite nanocrystals is maintained for 10 consecutive cycles without any visible degradation. The CHA zeolite (Si/Al = 2.1) reaches an almost perfect CO_2 storage capacity (8 CO_2 per unit cell) and high selectivity (no CH_4 was adsorbed according to IR spectroscopy).

The Precession Electron Diffraction Tomography (PEDT)$^{(3)}$ provided a refine structure of the nanosized CHA loaded with CO_2 (**Figure 1b** : *P*rojection of the refined structure along the <u>a</u> direction showing the localization of CO_2 molecules inside the super cage).

In summary, a method for the preparation of nanosized synthetic CHA-type zeolite without assistance of any organic structure directing agents is developed. CHA-type zeolite was characterized by FTIR, electron microscopy, NMR, and use of selective CO_2 capture.

Image 1:



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Biomedical Applications|Zeolites/Inorganic materials|Poster

FEZA21-OR-156

Assessment of nanosized zeolites to counteract hypoxia induced radio-resistance in glioblastoma

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Abstract Text:

One major feature of glioblastoma (GBM) is their pronounced resistance to conventional treatments, namely radiation therapy (RT) and chemotherapy (CT), mainly associated with their hypoxic nature. Indeed, in GBM, hypoxia is well pronounced and it is a markedly poor prognostic factor documented as an obstacle to the efficacy of radiation therapies. Therefore, strategies able to increase tumor oxygenation and/or increase sensitivity of tumor cells to radiation therapy are highly desired.

In recent years, nanosized materials have been used for a wide range of applications in medicine and biology. Among them, nanosized zeolites offer great advantage thanks to their small size well adapted to specifically target the tumor but also to their high flexibility offering possibilities to tune their chemical compositions and pores dimensions.

In this study, we present the use of nanosized zeolites to improve the oxygen and/or CO_2 delivery to target tumor cells. The applied strategy resulted in a considerable tumor oxygenation.

Precursor suspension of nanosized Na-Faujasite X (Na-X) zeolite was used as-synthesized and in ion -exchanged forms with gadolinium (Gd-X). We specifically focused on Gd-X nanozeolites since Gd is visible in MRI. In addition, zeolite nanocrystals with luminescent ruthenium-tris(2,2'-bipyridyl) complex ($Ru(bpy)_3$-FAU) were prepared as an intracellular tracing agent. The toxicity of zeolites was evaluated by analyzing cell viability, cell cycle and H2AX double strand breaks in DNA. In vitro study using U87-MG and U251-MG GBM cells and zeolite nanocrystals were performed. The U87-MG cells were also inoculated in right striatum of nude rats and the oxygenation under delivery of zeolite nanocrystals was measured using MRI.

The capacity of zeolites to release the oxygen payload was analyzed in aqueous solutions preliminary equilibrated at various O_2 concentrations in a hypoxic workstation to mimic the oxygen gradients observed in tumors. Incorporating scare amounts of gadolinium cations in the faujasite nanocrystals was found to improve the adsorption capacity for O_2 and CO_2 gases. Further we followed the biodistribution in the brain of intravenously injected nanozeolites and in the target tumor cells. The luminescent properties of ruthenium complex confined in the zeolite nanocrystals allow their instantaneous localization. The in vitro measurements on the U251-MG cells show that the nanozeolites were incorporated into the tumor cells mainly in the cytoplasm and lesser amount in their nuclei.

Finally, the in vivo tumor oxygenation using zeolites was analyzed. The ability of the nanosized zeolites to act as a vasoactive agent for a targeted re-oxygenation of the tumor after intravenous injection is demonstrated. The MRI results revealed that the nanozeolites are able to increase oxygenation and blood volume specifically within the brain tumor whilst no changes in the healthy non-tumoral brain were observed.

Our study demonstrated that nanosized zeolites are of great interest to target tumor cells due to their intracellular incorporation. Post-synthesis modification with gases improves their ability to carry hyperoxic gases and results in tumor reoxygenation.

Acknowledgements: Conseil Régional de Basse-Normandie (Projet Emergence ZEOXY), the European Union-Fonds Européen de Développement Régional (FEDER), the CNRS, the University of Caen Normandy and the Institut National du Cancer (INCA 11699).

Gas Adsorption, Separation and Storage|MOFs/Organic materials|Poster

FEZA21-OR-157

CO2 and SF6 adsorption on mixed-linker ZIF-7-8s: The effect of linker substitution on gas uptake and selectivity

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Abstract Text: A series of mixed-linker Zeolitic Imidazolate Framework(ZIF)-7–8s constructed from varying amounts of benzimidazolate (bIm) and 2-methylimidazolate (mIm) linkers are reported in this study. We demonstrate that the particle morphology and pore size of ZIF-7–8 can be tailored by carefully adjusting the ratios between bIm and mIm linkers in the frameworks resulting in a significantly enhanced CO_2 or SF_6 uptake capacity and selectivity. ZIF-7–8 containing 90% bIm and 10% mIm linkers were shown to have a CO_2 uptake capacity of 1.44 mmol g^{-1} at 293 K (1 bar) and a CO_2/N_2 selectivity of over 30. While ZIF-7–8 with 26% bIm and 74% mIm linkers had a SF_6 uptake of 2.08 mmol g^{-1} at 293 K (1 bar) and a high SF_6/N_2 selectivity of over 40. Isosteric enthalpy of adsorption calculations and cyclic pressure-swing adsorption experiments showed that both CO_2 and SF_6 were physisorbed on ZIF-7–8. The adsorption of CO_2 was also found to occur rapidly on all samples, with over 80% of the total uptake capacity being reached within 30 s. Detailed kinetics analysis concluded that the diffusion of CO_2 and SF_6 in the mixed-linker ZIF-7–8s were governed by a mixture of different mechanisms, including intracrystalline diffusion. The highly tunable sorption properties, uptake capacities and high gas selectivities of ZIF-7–8 render them as interesting candidate sorbents for certain greenhouse gases.

Catalytic Properties

FEZA21-OR-158

Mesoporous zeolites as versatile support for metal catalysts in industrially relevant reactions

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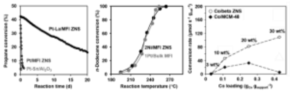
Abstract Text: Zeolites are widely used as acid catalysts and supports for metal catalysts in petrochemical industries. In particular, zeolites supporting noble metals, such as Pt and Ir, have shown high catalytic performance in hydrogenation/dehydrogenation, hydrocracking and oxidation reactions. Pt-group metals have high atomic polarizability and thus can readily be loaded inside zeolite micropores in the form of nanoparticles. When metals are well dispersed on zeolites as tiny nanoparticles, they exhibit markedly different physicochemical properties from those of the bulk metals, which are often highly attractive for catalytic applications. Due to the high cost of Pt-group metals, there have been many efforts to reduce the use of these precious metals, which can be largely categorized into: 1) alloying with other metal elements, and 2) replacement with inexpensive light metals, such as Ni and Co. However, controlling alloy formation within the narrow zeolite micropores has been quite challenging. Moreover, light transition metals are difficult to support as nanoparticles since they easily agglomerate to form large particles on the outer surface of zeolites due to their low polarizability.

In this presentation, we show that hierarchically meso-microporous zeolites with nanosponge-like morphology is an excellent support for both mono- and bimetallic catalysts in industrially relevant reactions (see Image 1). The mesoporous zeolite nanosponges (ZNS), synthesized using multi-ammonium surfactants as a meso-micropore dual structure-directing agent, is built with around 2 nm thick zeolite nanosheets stacked in a disordered manner. The ZNS exhibits high external surface area and uniform mesopore size, which can be controlled over the range of 2.5-6 nm by tailoring the length of the surfactant tail. First, it is shown that the formation of bimetal alloys of unprecedented compositions was enabled in mesopores of ZNS. Using ZNS as a support, we were able to obtain a Pt-rare earth intermetallic alloy catalyst in the form of Sub-3 nm-sized particles, which is hardly achieved via chemical route [1,2]. As Image 1a shows, the Pt-La nanoparticles supported on MFI ZNS (Pt-La/MFI ZNS) exhibits superior catalytic performance in propane dehydrogenation, as compared with those of Pt/MFI ZNS and conventional Pt-Sn/Al_2O_3 catalysts. Notably, the Pt-La/MFI ZNS catalyst exhibited much slower deactivation, where half of the initial activity (*i.e.*, conversion < 45%) was still maintained even after 20 days of reaction.

The next two examples show how the ZNS mesopores can be loaded with light metal elements, such as Ni and Co, which realized the replacement of expensive Pt. Image 1b presents the catalytic results of a 2 wt% Ni/MFI ZNS in *n*-dodecane hydroisomerization, as compared with 1Pt/Bulk MFI zeolite [3]. The catalytic activity of the Ni nanoparticles supported on MFI ZNS was comparable to those of the Pt supported catalysts even when the Ni loading was as low as 2 wt%, which was ascribed to the high Ni dispersion (< 6 nm). In the case of ZNS supporting Co metal, we show the advantage of mesopores in ZNS for loading a high amount of metal [4]. When the loading was increased from 3 to 30 wt%, the morphology of the supported Co changed from nanoparticles into nanowires in ZNS mesopores. Although the Co nanowires were sandwiched with mesopore walls, the surface of Co nanowires was still accessible through the zeolite micropore windows. The catalytic results of the Co/beta ZNS catalysts in Fischer-Tropsch synthesis (Image 1c) revealed the micropore-window effect of the Co/beta ZNS catalysts by higher CO conversion rates than those of Co/MCM-48 catalysts. We expect that our current explorations on metal catalysts supported on ZNS would help to open a new frontier in catalytic science, especially for practical catalytic applications in the near future.

Image 1:



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Novel Materials and Structural Methods

FEZA21-OR-159

JMZ-11: A Set of Non-Stochastic Intergrowths in the CHA-GME System with the Distinctive Feature of a Prominent “sfw-GME” Tail

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Abstract Text: JMZ-11 is a family of molecular sieves comprising intergrowths of *cha* and *aft* having an “*sfw*-GME tail”. This description is in terms of (layers of) cavities rather than layers of CHA and GME that is usual in the literature. The term “*sfw*-GME tail” represents the cavities of at least the length of the *sfw* cavity. The *gme* cavities that provide the support framework for cavities larger than *cha* are implicit in the model but omitted in the descriptions.

Control of the cavity distributions in JMZ-11 materials is realised using co-OSDA’s (US Patent 20200316572, 2020).

The “*sfw*-GME tail” can be visualised and the distribution sampled by electron microscopy. The parameters that describe the intergrowth are more readily quantified by analysis using *DIFFaX*[1] software to simulate the powder XRD pattern to match experiment. The combination of STEM and XRD is very powerful in the characterisation of planar defects in zeolites particularly in the case of JMZ-11.

DIFFaX modelling of CHA-GME intergrowths in the literature are based on the stacking of layers 5Å thick. These layers have a six ring on, say, the A site linked to another on, say, the B site. The stacking involves either a mirror 1.5Å above B site to yield ABBA…. or GME type stacking, or an inversion to yield ABBC…. or CHA type stacking. Structures in the literature appear to be either stochastic intergrowths of these layers, for example Babelite[2], or intergrowths of a limited number of cavity sizes such as SSZ-52[3].

JMZ-11 materials have a large volume fraction occupied by cavities of the size of *sfw* or larger (the “sfw-GME tail”) that are well represented by a monotonically decreasing distribution that follows the binomial representation. The proportions of *cha* and *aft* cavities do not conform to that distribution. A *DIFFaX* model with memory of the previous two layers (known as Reichweite 2) provides good representation of the powder diffraction patterns. The starting point for estimation of the 4 independent parameters in the model is obtained from analysis of the histograms of cavity distribution extracted from aberration-corrected STEM HAADF images of each sample. These parameters are readily interpretable and relate to the probability that a block of *cha* layers will form (q) and the average size of that block (p) and that a cavity larger than *aft* will form (s) and the average size of that cavity (r).

Four examples of JMZ-11 structures are described. JMZ-11A was prepared using N,N-dimethyl-3,5-dimethylpiperidinium cation (3,5 DMP) as OSDA[4] and has a large population of *cha* and *aft* cavities whilst 70% of the sample volume is in the *sfw-GME* tail. JMZ-11B, prepared using N,N-diethyl-2,6-dimethylpiperidinium cation (2,6 DMP)[4], has very low numbers of *aft* cavities lower even than umbers of *sfw* cavities. 65% of the sample volume is in the sfw-GME tail. JMZ-11C was synthesised by adding 1,3-bis (1-adamantyl) imidazolium cation (BAI) to the synthesis gel of JMZ-11A (Al_2O_3/BAI 0.10). BAI is a strong *aft* directing OSDA[5] and considerably bolsters the *aft* content relative to JMZ-11A such that *aft* cavities outnumber *cha* cavities. JMZ-11D was prepared by adding 1-adamantyl trimethylammonium cation (1-ATMAH) to the gel composition of JMZ-11A (Al_2O_3/1-ATMAH 0.003). 1-ATMAH favours *cha* cavities[6] and increases the *cha/aft* ratio relative to JMZ-11A. The *sfw*-GME tail accounts for 20% and 75% of the sample volume of JMZ-11C and JMZ-11D respectively. The results of molecular modelling of the binding energies of 1 or 2 of the OSDA’s in *cha, aft* and *sfw* cavities explain these distributions.

The performance of the materials in Cu-SCR of NO_x conversion is shown to be related to the ratio of chair and boat shaped 8-ring windows in the intergrowths.

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Catalytic Properties

FEZA21-OR-160

Shape selectivity effects in the conversion of multicyclic naphthenes

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Abstract Text: In the hydrocracking of paraffins by Pt-zeolite catalysts, the distribution of cracking products can be explained based on the structure of the reactant paraffin and the zeolite pore structure. The hydrocracking of cyclic compounds has been less intensively studied. Seminal works have shown that endocyclic cracking (the opening) of the last naphthene ring is difficult[1]. The dominating reaction pathway in substituted naphthenes with at least 10 carbon atoms is the Paring reaction, leading to isobutane and a smaller naphthene product.

However, the complexity of the reaction network increases exponentially when moving to larger polycyclic naphthenes, like decaline[2] or perhydrophenanthrene[3]. Such compounds are abundant in heavy oil fractions, i.e. in the feed of industrial hydrocracking processes. It is, therefore, crucial to improve our knowledge of how polycyclic naphthenes are converted depending on the zeolite structure. In the present contribution we analyze in detail, by using the high resolutive power of GCxGC-2D analysis, the product distribution of the tricyclic naphthene perhydrophenanthrene (PHP) over three acid catalysts: Pt/USY, Pt/Beta and Pt-ASA (Amorphous Silica Alumina). Shape selectivity effects were identified and interpreted by the help of Monte Carlo simulations.

The catalytic tests were carried out in a fixed bed reactor. The feed was phenanthrene diluted in n-heptane. A Pt/Al_2O_3 catalyst was placed on top of the Pt/Al_2O_3/zeolite catalyst in order to hydrogenate phenanthrene in situ, before contacting the feed with the acid catalyst. The reaction products were analyzed by GCxGC-2D. An MS and an FID detector were used in parallel, for identification and precise quantification of the reaction products (more than 300).

All three catalysts globally followed the same reaction pathways (Figure 1)[4]: ring-shift and ring-contraction PHP isomers were formed as primary products. They either converted into alkyladamantanes or into ring-opening products (ROP). The latter underwent cracking. The yield of ROP products was very low, indicating that cracking occurred rapidly after ring opening. Alkyladamantanes were not easily converted, due to their high thermodynamic stability. Although this scheme was common to all catalysts, the product distribution differed from one catalyst to another. We also underline that the main cracking products were C7 naphthenes, produced by a central cracking of ring opening products. The cracking to isobutane and decalin, which corresponds to the classical Paring mechanism, only played a very minor role. Beta was particularly selective to C7 products, while USY and ASA produced a broader cracking distribution (Figure 2).

This different behavior could be traced back to shape selectivity effects. The preferred PHP isomer over USY was a ring contraction product, while Beta mainly produced the ring-shift isomer perhydroanthracene (PHA). According to molecular simulations, this difference can be attributed to preferential adsorption of the linear PHA structure in the pores of Beta. PHA leads to different ring opening products than the ring-contration isomer. We could identify the ring opening isomers, which explain the very selective cracking to C7 naphthenes. Curiously, the behaviour of ASA resembled in certain aspects zeolite Beta and in others USY, indicating that some of the reactions over zeolite Beta are probably catalysed by its outer surface.

Overall, the study provides very useful insights in the hydroconversion of bulky naphthenes and how the choice of the acid catalyst can affect the obtained product distribution.

Image 1:

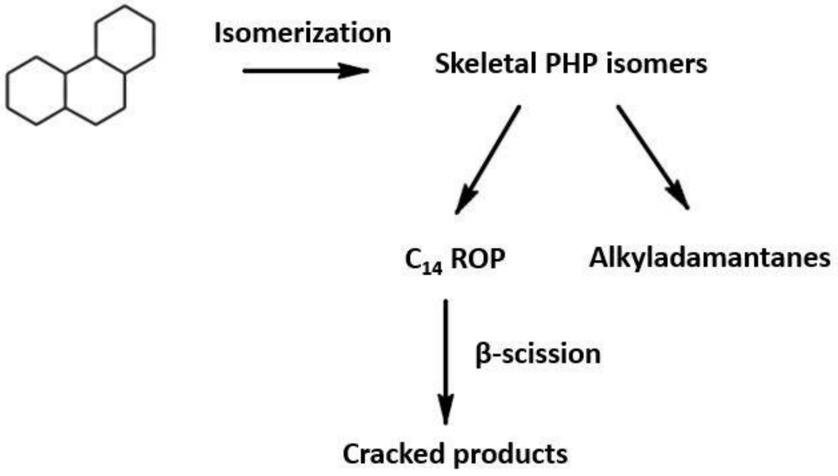
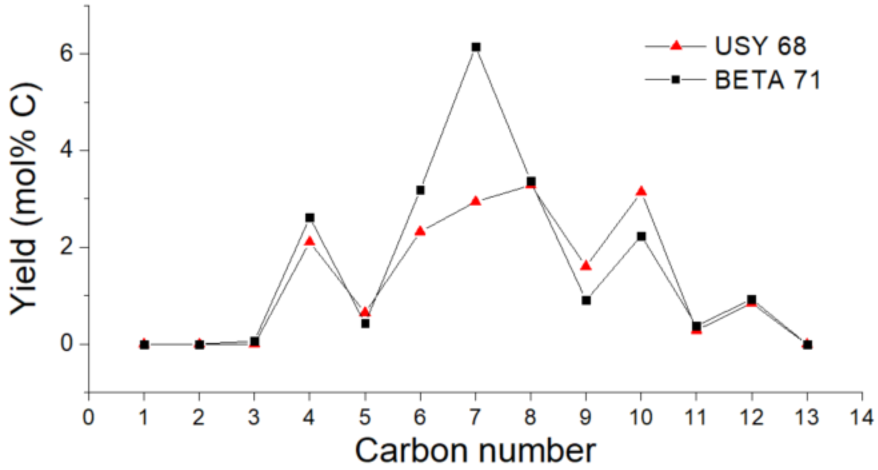


Image 2:



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