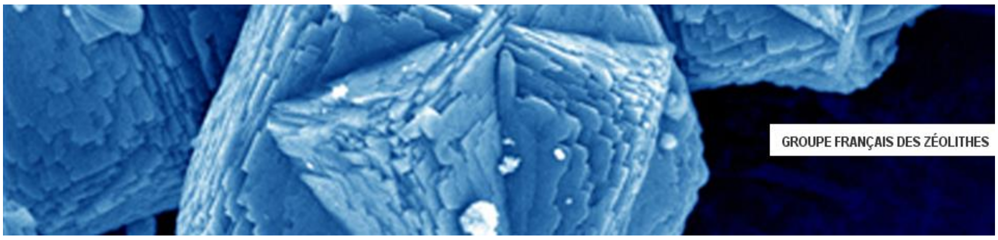
Groupe Français des Zéolithes

GFZ 2025



40th GFZ Meeting, 2nd International Edition, March 31st – April 3rd, 2025,

Blériot Plage VVF

For more details →

UCCS
UNITÉ DE CATALYSE
ET CHIMIE DU SOLIDE

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Monday 31st March

14h45	Bus from Calais Fréthun
15h15	Registration and posters installation
16h30	Opening Ceremony
16h45	Plenary: M. Tsapatsis
17h30	Short presentations and Exhibitors session
18h15	Free Time
19h30	Welcome Aperitif
20h00	Dinner

Tuesday 1st April

09h00	Plenary: V. Valtchev
09h45	O1.1. M. Alonso Doncel
	O1.2. M. Perbet
	O1.3 C. Marta
10h30	Coffee Break
11h00	O1.4. M. Froehly
	O1.5. M. Teixeira
	O1.6. M. Fahda
	O1.7. F. Di Renzo
	O3.1. C. Hewson
12h15	Lunch
13h45	Keynote: P. Horcajada
14h15	Short presentations session
14h45	Keynote: C. Volkringer
15h15	Poster session / Coffe Break
16h30	Free Time
18h30	Beer tasting event sponsored by the GFZ
20h00	Dinner

Wednesday 2nd April

09h00	Plenary: A. Mayoral
09h45	O3.2. S. Compère
	O3.3. M. El Zayed
	O3.4. B. Claessens
10h30	Coffee Break
11h00	O3.5. M. Gesvandtnerova
	O3.6. C. Longue
	O3.7. N. Al Hajjar
12h15	Lunch
13h45	Plenary: J. Rimer
14h30	O2.1. N. Chaouti
	O2.2. J. Cueto
	O2.3 M.T. Nogueira
15h15	Pause
15h45	Poster session / Coffe Break
17h00	Keynote: A. Wiersum
	O2.4 B. Zarbalyev
	O2.5. C. Grimaud
18h00	O2.6 M. Fabbiani
18h30	Aperitif and social event sponsored by Anton Paar
20h00	Banquet and social event sponsored by Anton Paar
22h00	Dance Party

Thursday 3rd April

09h00	O2.7 C. Ciotonea
	O2.8 F. Bihl
09h30	Keynote: Young Researcher Award 2025
10h15	General Assembly and Awards Ceremony
11h45	Bus for Calais Fréthun

40th GFZ Meeting, 2025

Scientific Programme

Monday 31st March 2025

15h15	Registration and posters installation
16h30	**Opening Ceremony**
Chair: Benoît Louis and Christophe Bouchy	
16h45	**Plenary:** "High Temperature and Pressure Zeolite Ammonia Adsorbents and Their Use in Adsorption-Enhanced Catalytic Reactors" **Michael Tsapatsis** (Johns Hopkins University)
17h30	**Short presentations Theme 1 (Synthesis and Shaping) and Exhibitors session**
P1-1	**Hydrodesulfurization of Thiophene over Ni doped MoS_2-supported mesoporous silica** J. Aguesse, A. Amedlous, F. Dalena, S. Mintova
P1-2	**Face-directed assembly of tailored isoreticular MOFs using centring structure directing agents** M. Barsukova, A. Sapianik, V. Guillerm, A. Shkurenko, A.C. Shaikh, P. Parvatkar, P.M. Bhatt, M. Bonneau, A. Alhaji, O. Shekhah, S.R.G. Balestra, R. Semino, G. Maurin, M. Eddaoudi
P1-3	**One-pot synthesis of Faujasite from natural clay via high pressure hydrothermal method** S.B. Gambo, N.P. Martin, C. Chassigneux, N. Dairou, V. Wernert
P1-4	**Shaped copper and cobalt-based MOFs decorated with graphene oxide: composites with improved hydrolytic stability and enhanced CO_2 adsorption** Y. Khadiri, A. Anouar, C. Volkringer, S. Royer, J. Dhainaut, A. El Kadib, T. Loiseau
EXH-1	**Ribori instrumentation**
EXH-2	**Mercer Instruments – Hiden**
EXH-3	**Anton Paar**
EXH-4	**Surface Measurement Systems**
EXH-5	**Microtrac**
EXH-6	**Micromeritics**
18h15	Free Time
19h30	*Welcome Aperitif*
20h00	*Dinner*

Tuesday 1st April 2025	
Chair: Louwanda Lakiss and Alexander Sachse	
09h00	**Plenary:** "Extra-Large Pore Zeolites: A Paradigm Shift" **Valentin Valtchev** (ENSICAEN)
09h45	**Oral 1 Theme 1**: **M. Alonso-Doncel,** B. Fodor, P. Horcajada, D.P. Serrano: "Second-Generation Dendritic MFI Zeolites: Synthesis through a Rapid, Efficient, and Versatile Procedure"
10h00	**Oral 2 Theme 1**: **M. Perbet,** E.A. Quadrelli , D. Farrusseng, A. Bonhommé, M. Martin: "Exploring the growth mechanisms in a green Al-fumarate synthesis"
10h15	**Oral 3 Theme 1**: **C. Marta,** A. Le Valant, S. Loridant, A. Sachse: "Innovative Templating Agent For SAPO-34 Nanosheets: A Strategy To Overcome Diffusion Limitations In Catalytic Processes"
10h30	*Coffee Break*
Chair: Louwanda Lakiss and Andrey Ryzhikov	
11h00	**Oral 4 Theme 1**: **M. Froehly,** G. Chaplais, H. Nouali, V. Roucoules, F. Payet, T.J. Daou: "MOF A520 in pharmaceutical packaging: safeguarding drugs from humidity"
11h15	**Oral 5 Theme 1**: **M. Teixeira,** R.A. Maia, B. Louis, S.A. Baudron: "Urea-based solvents for Metal-Organic Framework synthesis"
11h30	**Oral 6 Theme 1**: **M. Fahda,** Y. Sun, P. Lu, V. Valtchev: "ZMQ-1: A stable 28-membered ring three-dimensional aluminosilicate zeolite"
11h45	**Oral 7 Theme 1**: J.F. Sierra-Cantor, O. Gimello, A. Aubert-Pouëssel, C.A. Guerrero-Fajardo, **F. Di Renzo,** N. Tanchoux, C. Gérardin: "Recrystallized micro-mesoporous ferrierite for best biofuel production"
12h00	**Oral 1 Theme 3**: **C. Hewson,** S. McIntyre, A. Hanif, L. Sun, D.R. Williams, P. Iacomi: "Evaluating the influence of stream contaminants on the carbon capture potential of prototypical porous materials"
12h15	*Lunch*

Chair: Emily Bloch and Alexandre Legrand	
13h45	**Keynote:** "Metal Organic Frameworks: Water-Related Applications" **Patricia Horcajada** (IMDEA)
14h15	**Short presentations Theme 2 (Applications for the environment, Energy and Health) and Theme 3 (Characterization and Modeling) session**
P2-1	**Valorisation of Greenhouse and Acid Gas by Low-Silica Zeolite Catalyst** S.R. Batool, M. Fabbiani, L. Pinard, A. Novikov, H. Retot, V. Valtchev
P2-2	**A Versatile Cerium MOF with 1-D Open Metal Sites for Catalysis** S. Feyziyeva, N. Israfilov, B. Louis

P2-3	**Nano zeolite-based polyamide composite membrane for desalination** S.Wei, H. Guo, V. De Waele
P2-4	**Tuning Co^0/CoO ratios of Co/MFI catalysts for CO_2 hydrogenation to ethanol via zeolite framework tetrahedral aluminum** X. Ding, X. Liu, V. de Waele
P2-5	**Investigating the impact of monovalent alkali metal incorporation on the properties of ZSM-5 zeolites** S. Dong, B. Louis
P3-1	**Machine Learning Perturbation Theory for an accurate prediction of adsorption enthalpies and activation energies in zeolites** M. Badawi, B. Herzog, J. Rey, D. Rocca, C. Chizallet, T. Bučko
P3-2	**Real time tracking of Gallium oxides in MFI zeolites during pretreatment by infrared operando** T. Lemaitre, L. Cardenas, S. Moldovan, P. Bazin, A. Vicente, C. Canaff, K. Thomas, L. Pinard
P3-3	**The impact of templates on the properties of porous materials** E. Dib, L. Pace, V. Sarou-Kanian, D. Honorato-piva, F. Dalena, S. Mintova
14h45	**Keynote:** "Synthesis and functionalization of porous materials for the decontamination of SARS-CoV-2 and other enveloped viruses" **Christophe Volkringer** (UCCS)
15h15	Poster session / *Coffee Break*
16h30	Free Time
18h30	*Beer tasting event sponsored by the GFZ*
20h00	*Dinner*

Wednesday 2nd April 2025	
Chair: Valentin Valtchev and Rémy Guillet-Nicolas	
09h00	**Plenary:** “Revealing Zeolite structural Intricacies: Advanced Insights with Modern TEM Methods” **Alvaro Mayoral** (INMA)
09h45	**Oral 2 Theme 3**: **S. Compère,** A. Le Person, A. Moissette, H. Vezin, I. Batonneau-Gener, A. Sachse: “From Solid Precursors to Zeolite-Templated Carbon: A Molecular Odyssey Toward Porous Carbon Frameworks”
10h00	**Oral 3 Theme 3**: **M. El Zayed,** P. Bazin, L. Pinard: “Zeolite's positive role in platinum-catalyzed hydrogenation: Evidence from high-throughput infrared studies”
10h15	**Oral 4 Theme 3**: **B. Claessens,** M.A. Benchaabane, M. Levy, G. Trierweiler Gonçalves, J.L. Paillaud, G. Chaplais, E. Bloch, S. Bourrelly: “Cation-Exchanged LTA Zeolites for Propane / Propylene Separation”
10h30	*Coffee Break*
Chair: Alvaro Mayoral and Alexander Sachse	
11h00	**Oral 5 Theme 3**: **M. Gešvandtnerová,** P. Raybaud, C. Chizallet, T. Bučko: “Isobutanol to linear butenes: Unravelling competing catalytic reactions sharing a common transition state through Blue moon sampling”
11h15	**Oral 6 Theme 3**: R. Zhang, B. Wang, J. Xu, H. Liu, H. Zhao, J. Wang, S. Xu, F. Dalena, **C. Longue,** N. Chaouati, B. Louis, L. Pinard, Z. Qin, X. Gao, S. Mintova: “New synthesis route for Y/ZSM-5 zeolites: Validated through model reactions”
11h30	**Oral 7 Theme 3**: **N. Al Hajjar,** T. Roland, Y. Wang, A. Khodakov, V. De Waele: “Ultrafast Femtosecond Laser Spectroscopy Of Heterogeneous Solid Photoactive Catalysts For The Conversion Of Methane”
12h15	*Lunch*

Chair: Benoît Louis and Christophe Bouchy	
13h45	**Plenary:** “Elucidating and Controlling Zeolite Crystallization for the Design of Advanced Materials” **Jeffrey D. Rimer** (University of Houston)
14h30	**Oral 1 Theme 2**: **N. Chaouati,** Mohammad Fahda, S. Mintova, L. Pinard, V. Valtchev: “Catalytic Potential of Extra-Large Pores ZEO-1 Zeolite”
14h45	**Oral 2 Theme 2**: G. Pérez-Martín, **J. Cueto,** M.M. Alonso-Doncel, M. Paniagu, G. Morales, J. A. Melero, D.P. Serrano: “Enhanced Furfural Conversion into γ-Valerolactone and Isopropyl Levulinate over Catalysts based on Dendritic ZSM-5 Zeolite Modified by ZrO$_2$”

15h00	**Oral 3 Theme 2**: **M.T. Nogueira,** F. Lemos, A.C. Marques, M.A.N.D.A. Lemos: "Assessing Zeolites as Catalysts for Biaxially Oriented Polypropylene (BOPP) Chemical Recycling"
15h15	Poster session / *Coffee Break*

Chair: Emily Bloch and Julien Grand	
17h00	**Keynote:** "The use of zeolites in the production of lower emission fuels" **Andrew Wiersum** (ExxonMobil)
17h30	**Oral 4 Theme 2**: **B. Zarbaliyev,** Narmina Guliyeva, G. Lutzweiler, B. Louis: "Injectable chitosan-nanozeolite hydrogels as cation carriers for chronic wounds"
17h45	**Oral 5 Theme 2**: **C. Grimaud,** C. Daniel, A. Tuel, A. Mesbah, D. Farrusseng: "Roles of cation location in LTA zeolite for methane storage"
18h00	**Oral 6 Theme 2**: **M. Fabbiani,** S.R. Batool, L. Pinard, R. Ghassemi, S. Zare Ghorbae, J. Lauwaert, J. Thybaut, V. Valtchev: "Acid gas valorisation on Na-Faujasite: catalytic COS formation"
18h30	*Aperitif and social event sponsored by Anton Paar*
20h00	*Banquet and social event sponsored by Anton Paar*
22h00	*Dance Party*

Thursday 3rd April 2025	
Chair: Louwanda Lakiss and Benoît Louis	
09h00	**Oral 7 Theme 2**: **C. Ciotonea,** M. Mohamad Ali, M. Chaghouri, L. Tidahy, M. Marinova, E. Abi-Aad, C. Gennequin, S. Royer: " How is the promoter influencing the stability of Ni based catalyst for dry reforming of methane?"
09h15	**Oral 8 Theme 2**: **F. Bihl,** B. Louis, A.C. Roger: " How to enhance a catalytic reaction process by using zeolite and MOFs as sorbents?"
09h30	**Keynote: Young Researcher Award 2025**
10h00	**General Assembly and Awards Ceremony**
11h45	**Bus for Calais-Fréthun Train Station**

PLENARIES

THEME Theme 2: Applications for the environment, energy, and health

High Temperature and Pressure Zeolite Ammonia Adsorbents and Their Use in Adsorption-Enhanced Catalytic Reactors

Nayeon Kang, Juan C. Muñoz-Senmache, Prerna, Zihao Rei Gao,Cristian Aristizabal-González, Jesse Prelesnik, Hsiao-Feng Liu, Paul Haghi Ashtiani, Ronaldo Pangestu Hadi, Maxime A. Siegler, Chao Wang, Brandon C. Bukowski, Arturo J. Hernández-Maldonado, J. Ilja Siepmann, **Michael Tsapatsis**

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University of Puerto Rico Mayagüez Campus, Mayagüez, Puerto Rico 00680, USA.
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Improving the efficiency of ammonia synthesis processes by integrating reaction with separation is a topic of long-standing interest. One approach is the use of sorption-enhanced catalytic reactors, where in situ ammonia sorption removes it from the vapor phase and allows reaction to proceed with ammonia yields beyond those dictated by thermodynamic equilibrium in the absence of sorption. While many sorbents have been used for this purpose, challenges remain with full regeneration at practical ammonia pressures limiting the potential benefits of sorption-enhanced reactors. Moreover, experimental data on NH_3 adsorption at high pressure are scarce and necessary to properly evaluate NH_3 adsorption as a possible and viable separation option. In this talk, I will summarize progress in a collaborative effort on high pressure ammonia adsorption in microporous solids and their integration in sorption enhanced reactors.

Extra-Large Pore Zeolites: A Paradigm Shift

Valentin Valtchev

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Expanding zeolite channel sizes has long been a critical challenge in enhancing their functionality for processing bulky molecules. Conventional zeolites with 12-membered ring (12MR) pore openings are limited by their inability to accommodate larger molecules, while ordered mesoporous materials face constraints due to their amorphous structures, low hydrothermal stability, and weak acidity, hindering industrial adoption.

This presentation offers an overview of the development of extra-large pore zeolites, focusing on thermally stable (alumino)silicate frameworks that exceed the 12MR pore system. Key factors influencing their formation, including building units and organic structure-directing agents, will be discussed. The highlight is ZMQ-1, the first mesoporous zeolite featuring 2.3 nm channels.

We detail the physicochemical properties of ZMQ-1, characterized using in situ FTIR spectroscopy, solid-state NMR, and argon adsorption. Its catalytic performance in vacuum gas oil cracking is benchmarked against existing molecular sieve catalysts, demonstrating significant potential for industrial applications. These findings offer new insights into the design and application of extra-large pore zeolites, emphasizing their relevance for future advancements in zeolite science and technology.

Furthermore, ZMQ-1 introduces a novel class of zeolitic materials, combining intrinsic mesoporosity, structural robustness, and inherent acidity. This discovery redefines zeolite application possibilities and inspires the development of next-generation mesoporous zeolites for process industries.

Revealing Zeolite structural Intricacies: Advanced Insights with Modern TEM Methods

Alvaro Mayoral[1]

[1] *Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza, Zaragoza 50009, Spain.*

Abstract: Transmission Electron Microscopy (TEM) plays a pivotal role for investigating the structural and morphological characteristics of all kinds of nanomaterials. In the field of nanoporous solids, particularly zeolites, TEM has advanced, from the basic examination of the crystal morphology, to the image contrast analysis, pore identification up to the single atom exploration. In this talk, we will delve into the background and recent advancements in TEM techniques tailored for the characterization of zeolites[1, 2]. We will explore the challenges associated with imaging and analyzing zeolite structures at the nanoscale, including issues related to electron beam damage and resolution limitations. Subsequently, it will be highlighted the methodological advancements in TEM, mainly focusing on high-resolution imaging techniques and how it has enabled to probe the intricate pore architectures of zeolites with unprecedented detail, providing valuable insights into their synthesis, structure-property relationships, intergrowths and growing mechanisms[3, 4]. Alongside, it will be described how image resolution is diminished due to the low signal-to-noise (SNR) ratio, associated to the high instability of zeolites under the electron beam (e-beam), suffering from the low collection efficiency of the detectors and the low number of electrons used to form the images.

Finally, the recent technological advancements and image analysis techniques designed to enhance spatial resolution and sensitivity while minimizing beam damage will be discussed. These include low-angle annular dark field (LAADF), annular bright field (ABF), differential phase contrast imaging (DPC), and 4D-STEM through ptychography. These methods provide a detailed characterization of nanoporous solids, revealing their atomic-level structure. Many of these techniques can be combined, sometimes even simultaneously, enabling a multimodal approach for a more comprehensive understanding of zeolite materials.

Overall, this presentation aims to showcase the transformative role of TEM in advancing our understanding of nanoporous solids, with a specific focus on zeolites.

Acknowledgements: The Spanish Ministry of Science (RYC2018-024561-I; CNS2023-144346, MMT24-INMA-01), Gobierno the Aragon (Nanomidas group, code E13_23R), the Spanish National Research Council (CSIC) through the i-COOP program (COOPB23035), National Facility ELECMI ICTS node "Laboratorio de Microscopías Avanzadas" at the University of Zaragoza and to the Centre for High-resolution Electron Microscopy, CħEM, School of Physical Science and Technology, ShanghaiTech University (#EM02161943).

References:

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(2) Li, C.; Zhang, Q.; Mayoral, A. Ten Years of Aberration Corrected Electron Microscopy for Ordered Nanoporous Materials. *Chem. Cat. Chem.* **2020**, *12*, 1248-1269.

(3) Terasaki, O.; Ohsuna, T. TEM study on zeolite fine structures: homework from Cambridge days. *Topics in Catal.* **2003**, *24*, 13-18.

(4) Lee, H.; Shin, J.; Lee, K.; Choi, H. J.; Mayoral, A.; Kang, N. Y.; Hong, S. B. Synthesis of thermally stable SBT and SBS/SBT intergrowth zeolites. *Science* **2021**, *373* (6550), 104-107. DOI: 10.1126/science.abi7208 %J Science.

Elucidating and Controlling Zeolite Crystallization for the Design of Advanced Materials

Jeffrey D. Rimer
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This talk will address recent progress in the understanding of zeolite growth mechanisms and how the knowledge gained from these studies can be used for the rational design of catalysts for diverse reactions of commercial significance. The complex pathways of zeolite crystallization make it difficult to control their physicochemical properties.[1, 2] This talk will highlight several methods that can be used to tailor zeolite crystal size, morphology, and composition in ways that reduce diffusion limitations, tune acidity, and selectively control acid siting to enable the development of catalysts with superior performance compared to materials obtained by conventional synthesis routes. Examples include the use of seed-assisted syntheses and interzeolite transformations[3], the design of coreshell and zoned materials[4, 5], self-pillared zeolites[6], and a new class of zeolites referred to as finned materials that have been demonstrated for diverse structures.[7] Direct comparisons of ZSM-5 catalysts under identical reaction conditions using methanol to hydrocarbons as a benchmark reaction has revealed the presence of intrinsic defects in MFI-type materials related to several factors, including the nature of aluminum sites. Another subject that will be discussed in this talk is the replacement of aluminum with heteroatoms that can be integrated in both conventional and hierarchical zeolites to enhance catalyst performance.[8] Examples include the synthesis of finned zeolites using seeded growth to introduce fin-like protrusions with identical crystallographic registry as the interior crystal. Introduction of various heteroatoms (e.g., Ga, Ti) into zeolites is a strategy for tailoring zeolite acidity for a broad range of reactions, while these sites can also be used as sacrificial placeholders for post-synthesis removal as a means of defect engineering. Many of these approaches transform materials into pseudo-nanoparticles with improved mass transport and dramatically enhanced catalyst performance.

References

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8. Abutalib, A., D. Parmar, J. Kim, and J.D. Rimer, *Pairing Ga/Al-Zeolites with tailored acidity as tandem catalysts for the conversion of alcohols to olefins.* Journal of Catalysis, 2024. **433**.

KEYNOTES

METAL ORGANIC FRAMEWORKS: WATER-RELATED APPLICATIONS

Patricia Horcajada

Advanced Porous Materials Unit, IMDEA Energy Institute, 28935 Móstoles-Madrid, Spain

Although water is considered a renewable resource by rainfall, its availability is finite in terms of time and location. Closely associated with the overall availability of water is the problem of water pollution and human diseases. Of particular concern are the emerging organic contaminants, including pharmaceuticals, pesticides, veterinary products, or plastics, among others. These pollutants can severely affect the environment as well as the animal and human health.[1] Despite several strategies have been proposed for the EOCs exclusion, their insufficient removal of these processes in wastewater treatment plants (WWTPs) makes necessary to search new efficient alternatives for water remediation.

Similarly, disinfecting water is one of the most important processes in drinking water treatment plants (DWTPs) to control waterborne diseases transmission. Chlorination is the most commonly used process but it could lead to the formation of hazardous inorganic by-products (ClO_2^- and ClO_3^-).[2]

In this context, metal-organic frameworks (MOFs) have emerged as promising candidates for water treatment.[3] Here, some recent examples of their performances on challenging topics will be presented, including: i) plastic degradation, ii) pharmaceuticals removal in wastewater; iii) fuel cells and electrolyzers; and, iv) purification of disinfected potable water.[4]

Acknowledgments. H2-MOF project (TED2021-132092B−C21 funded by MCIN/AEI/10.13039/501100011033), CLORATOS-CM (IND2019/AMB-17129) and CMOFs4water-CM (ref: TEC-2024/ECO-332).

References

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THEME Theme 2: Applications for the environment, energy, and health

Synthesis and functionalization of porous materials for the decontamination of SARS-CoV-2 and other enveloped viruses.

Christophe VOLKRINGER[a]

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For several years, the world population has been under the threat of deadly epidemics for which vaccines do not exist or are still being developed (e.g. SARS CoV-2, Ebola) and the resurgence of infectious diseases that were thought to be under control (whooping cough, tuberculosis, measles, etc.). Although the reasons for this proliferation are sometimes still poorly understood, they are often the result of a combination of factors involving poverty, distrust of vaccination, climate change or the weakening of the immune protection of populations.

This talk will be dedicated to our recent works about the use of porous materials (Metal-Organic Frameworks and silica) for the decontamination of enveloped viruses. Most of the materials presented in this talk were tested against two highly virulent coronaviruses, SARS-CoV-2 and MERS-CoV, and against hepatitis C virus (HCV).

A first series of results will concern the use of porphyrin ligands as building blocks for MOFs (Al-TCPP, PCN22n) and their impact on the studied viruses (Fig. 1).[1] Then, archetypal silica and MOFs were functionalized with different photosensitizers via the formation of robust amide groups.[2] The virucidal activity of these materials was superiorly enhanced with this way, compared to the non-functionalized materials.

For both studies, the mechanism of action leading to very high antiviral activities (reduction of the viral titer by >99.9%) will be discussed.

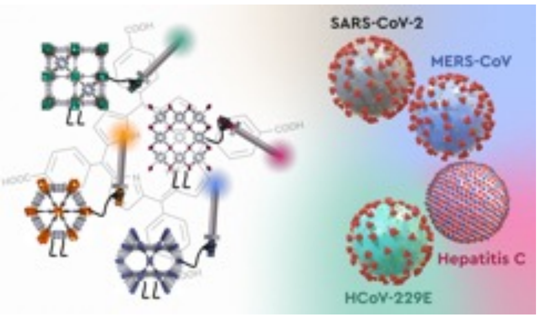

Fig. 1. Illustration of the antiviral activities of MOFs on examples of enveloped viruses.

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2. *Submitted*

THEME

☐ Theme 1 : Synthesis and shaping
☒ Theme 2: Applications for the environment, energy, and health
☐ Theme 3 : Characterization and modeling

The use of zeolites in the production of lower emission fuels

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Lower Emissions Fuels (LEF) will be required to meet the CO2 emissions mitigation ambitions of the world, driven by evolving regulations. Innovation, use of proven or scalable technology, and lower system cost will be key elements for potential solutions. LEF can be made using a variety of different feedstocks in combination with various established and/or new processes and catalysts.

In this presentation, we will be discussing various LEF technologies involving the use of zeolites in the production of gasoline and sustainable aviation fuel (SAF) from renewable methanol (MeOH). Renewable MeOH, as a versatile and lower carbon intensity intermediate, is anticipated to be produced in greater volumes during the energy transition and can serve as a building block for the conversion of renewable electricity to LEF (power-to-liquids). The opportunities for tailoring the yield of specific molecules and further reducing capital cost and carbon intensity (CI) by adjusting the combination of catalyst, configuration and process conditions will be elaborated upon to provide insights on future R&D directions in the commercialization of renewable MeOH conversion technologies.

ORALS

THEME

☒ Theme 1 : Synthesis and shaping

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☐ Theme 3 : Characterization and modeling

Second-Generation Dendritic MFI Zeolites: Synthesis through a Rapid, Efficient, and Versatile Procedure

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ZSM-5 zeolite with dendritic morphology at the nanoscale has been reported in 2023[1], marking a significant advancement in terms of accessibility and catalytic performance compared with other zeolites with enhanced accessibility. This improvement arises from their unique morphology, consisting of a radially oriented aggregation of branched nanounits, forming oval-shaped particles measuring approximately 800 nm in length and 450 nm in width (Figure 1.a). The synthesis method involved the preparation of a pre-crystallized synthesis gel, where protozeolitic units were first formed, followed by the addition of an amphiphilic silanizing agent[2]. This silanized gel was subjected to hydrothermal crystallization at 150–170°C for times typically ranging from 5 to 7 days, with the synthesis occurring via a micelle-templated mechanism.

In this work, we present a modified synthesis methodology of dendritic MFI zeolites using a silanized silica xerogel as the raw material, impregnated at incipient wetness with an aqueous TPAOH solution. Metallic cations can be incorporated either in the xerogel or in the impregnating solution. This approach yields spherical particles with diameters around 200 - 250 nm, consisting of a dendritic array of small nanounits (c.a. 5 nm). Core-shell configurations are obtained when starting from metal-containing xerogels (Figure 1.b), whereas very open dendritic nanoarchitectures are formed if the metallic species are added in the wetness impregnation step. This strategy has been successfully applied to produce a second generation (2G) of MFI dendritic zeolites that incorporate aluminum, gallium, or iron into the zeolitic framework (Figure 1.c). This new synthesis methodology has drastically reduced the volume of the synthesis gel and shortened the crystallization time to just 1 day. Moreover, it has also significantly improved the synthesis yield, increasing from approximately 50% to 98%, and the metal incorporation efficiency, rising from 75% to 99%. Relevant improvements have been also denoted for the 2G dendritic MFI zeolites in terms of accessibility and catalytic performance in different reactions.

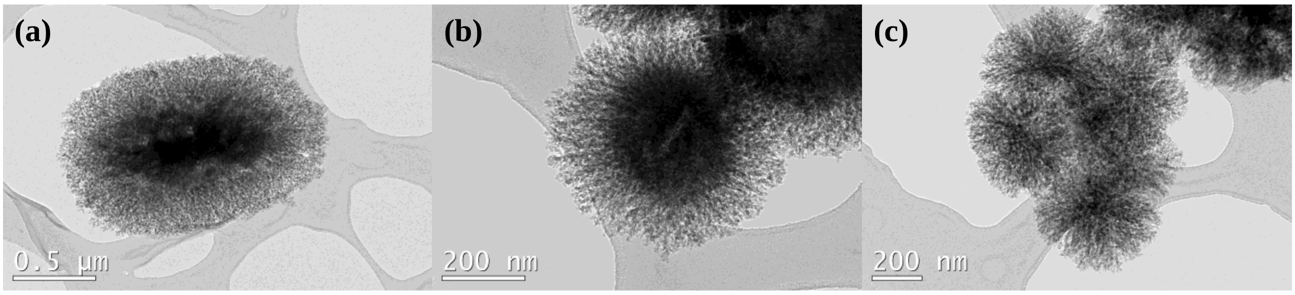

Fig. 1. TEM micrographs of: 1G dendritic ZSM-5 zeolite (a), 2G dendritic ZSM-5 zeolite synthesized from a silanized silica-alumina xerogel (b), and 2G dendritic ZSM-5 zeolite synthesized from a silanized silica xerogel using an Al-containing impregnation solution (c).

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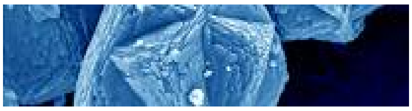

THEME

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Exploring the growth mechanisms in a green Al-fumarate synthesis

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Deep understanding of MOF synthesis mechanisms remains elusive. Indeed, MOFs exhibit a wide variety of structures, leading to diverse nucleation and growth mechanisms. During synthesis, it is common for intermediate and/or metastable phases to form[1]. Studying these complex and varied crystallization processes is therefore a significant challenge. As a result, the mechanisms behind MOF formation remain poorly understood. Consequently, it is necessary to combine multiple *ex situ* and *in situ* characterization methods and cross-analyse the resulting data to propose comprehensive hypotheses on MOF growth.

In this study, we aimed to understand the growth mechanisms of aluminium fumarate using a water-based green synthesis approach. Unlike previously reported aqueous-phase synthesis routes, which require basic conditions (e.g., NaOH addition[2]), the method presented here operates at a pH below 3. The use of aluminium isopropoxide as a precursor allows for a controlled reaction with fumaric acid without requiring pH adjustment.

Raman spectroscopy is particularly useful for studying interactions in aqueous solutions due to its relative insensitivity to water vibrations[3]. To identify the spectral bands in the *in-situ* measurements, all reference spectra of the reactants and products were first acquired individually. Subsequently, the spectral bands of the precursors, intermediate species, and final products were recorded *in situ* at 70 °C. At this temperature, the bands are sufficiently pronounced to be reliably identified and monitored over time (example of results Figure 1). For monitoring aluminium fumarate formation via Raman spectroscopy, four key bands were tracked: 780, 909, 1010 and 1590 cm⁻¹.

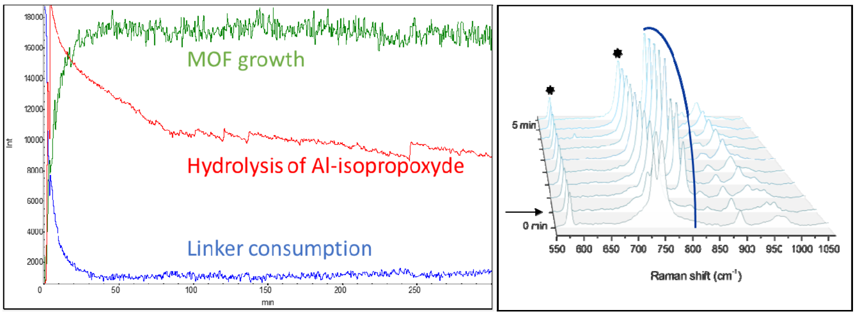

Fig. 1. Time resolved follow of three Raman bands during synthesis (left) and evolution of a Raman band associated to aluminium isopropoxyde hydrolysis over 5 minutes (right).

This work provides insights into the growth mechanisms of aluminium-based MOFs and could pave the way for the development and understanding of other aluminium-containing MOFs.

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Innovative Templating Agent For SAPO-34 Nanosheets: A Strategy To Overcome Diffusion Limitations In Catalytic Processes

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SAPO-34 zeotypes are widely used in OX-ZEO catalysts due to their well-documented high performance in the methanol-to-olefin (MTO) reactions [1]. These zeotypes with the CHA topological structure - comprised of large cavities and small 8-ring pores - show moderate acidity and high hydrothermal stability, but can suffer rapid deactivation due to retained organic species within the large CHA cavity [1]. Since deactivation is closely linked to diffusion limitations, reducing crystal size to the nanoscale has proven to be an effective strategy to address this challenge. Smaller crystals shorten the diffusion path length, allowing for more efficient utilization of active sites and improving catalytic activity, selectivity, and stability [2,3]. Nevertheless, nanosized zeolites present practical challenges, such as increased pressure drop and difficulties in recyclability, which hinder their broader application. An innovative solution to these issues involves designing nanosheet-based SAPO-34 structures that assemble into micron-scale particles. This approach combines the advantages of nanoscale diffusion efficiency with the structural benefits of larger, more manageable particles.

In this study, we introduce an alternative synthesis route employing a novel templating agent to produce nanosized SAPO-34 zeotypes in a cost-effective and straightforward manner. The resulting materials feature well-defined nanosheets approximately 5 nm in thickness (Figure 1a), contrasting with the conventional cuboid morphology of SAPO-34. The nanoscale crystal size was confirmed by calculating the coherent crystallization domains from the XRD pattern (Figure 1b). Preliminary catalytic studies in the OX-ZEO process demonstrate promising results, underscoring the potential of these materials for advanced catalytic applications.

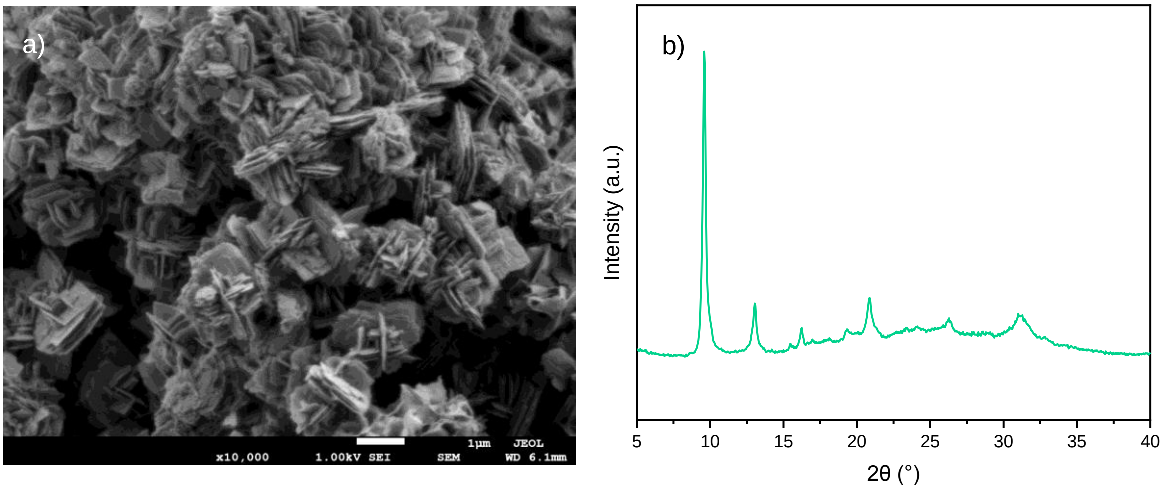

Fig. 1. a) SEM analysis shows the morphology of the nanosheet SAPO-34 obtained when using a novel templating agent; b) XRD pattern of nanosheet SAPO-34.

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THEME

☒ Theme 1 : Synthesis and shaping
☐ Theme 2: Applications for the environment, energy, and health
☐ Theme 3 : Characterization and modeling

MOF A520 in pharmaceutical packaging: safeguarding drugs from humidity

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Moisture-sensitive drugs require innovative packaging solutions to improve their shelf life and maintain their efficiency. The microporous material MIL-53(Al)_FA, also known as MOF A520, has emerged as a promising candidate for this application due to its high water adsorption capacity (452 mg $_{\text{water}}$/g $_{\text{MOF A520}}$), thermal stability and low production cost [1]. However, MOF A520, obtained in powder form, requires shaping for industrial applications. To address this issue, Aptar CSP Technologies developed a 3-phases composite formulations (main polymer + channelling agent + porous material) designed for the extrusion/injection manufacturing of pharmaceutical packaging [2]. In this work, the microporous zeolite 4A, used in the already commercialized 3 phases formulation, was advantageously substituted by MOF A520 to produce granulates, injection molded parts and films with higher water adsorption capacities (Fig. 1).

Thus, MOF A520 was incorporated into the polymer matrix with a loading rate ranging from 29 to 55 wt.%. The characterization of composites by XRD, TGA and SEM-EDX highlighted the preservation of the crystalline structure and thermal stability of the MOF A520, as well as a homogeneous particles distribution within the polymer matrix. Water vapor adsorption experiments, carried out on the MOF A520-based composites in a climatic chamber at 22 °C and 80 % relative humidity (RH), showed that water adsorption capacities reaching up to 85 % of the powder's capacity. In addition, the adsorption kinetics can be modulated by the loading rate, the amount of channelling agent, the shape and the thickness of the composite film. The control of these properties by the fine adjustment of the manufacture parameters make possible the development of a wide range of active packaging solutions, improving the preservation of pharmaceutical products, thus reducing their loss while guaranteeing patient safety.

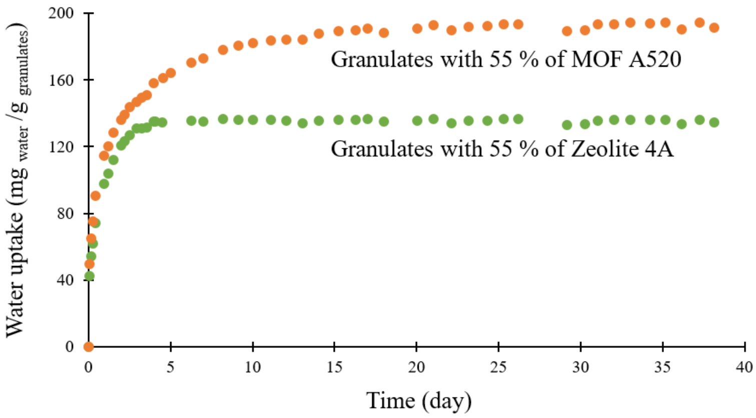

Fig. 1. Water adsorption kinetics of MOF A520 and 4A zeolite granulates composites at 22 °C and 80 %RH

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THEME

☒ Theme 1 : Synthesis and shaping
☐ Theme 2: Applications for the environment, energy, and health
☐ Theme 3 : Characterization and modeling

Urea-based solvents for Metal-Organic Framework synthesis

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Urea-based solvents represent an emerging class of alternative media for the preparation of Metal-Organic Frameworks (MOFs). For example, ionothermal synthesis using Deep Eutectic Solvents (DESs) of the choline chloride/urea derivative type has demonstrated its ability to yield porous materials with a noticeable impact on crystal morphology, textural properties and chirality [1-2]. Alternatively, the urothermal method consisting in using molten urea-based species as solvents has also shown great promises [3]. In this context, we are investigating the potential of these two synthetic methods for the elaboration of MOFs with a particular focus on alkaline earth MOFs as these are less toxic and often exhibit important CO_2 sorption capabilities [4].

Following our work on the impact of DESs on the synthesis of Mg-MOF-74 [5], the synthesis of novel alkaline earth MOFs in ethylene urea-based systems was studied [6]. Depending on the cation, the ligand and the nature of the solvent used, various new architectures could be obtained. Interestingly, many of these structures are based on the same pillar, in which ethylene urea is bridging metallic cations. Taking advantage of this recurring secondary building unit, we attempted to engineer new porous materials. These results, as well as more recent advances, will be presented in this contribution.

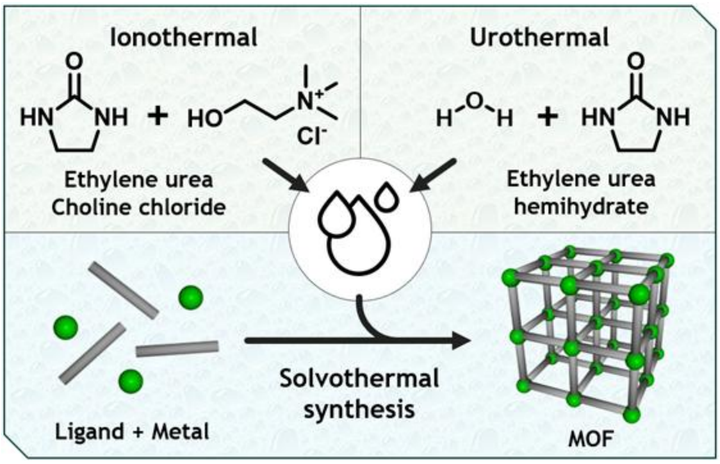

Fig. 1: Ionothermal and urothermal syntheses for the preparation of MOFs

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THEME

☐ Theme 1 : Synthesis and shaping

☐ Theme 2: Applications for the environment, energy, and health

☒ Theme 3 : Characterization and modeling

ZMQ-1: A stable 28-membered ring three-dimensional aluminosilicate zeolite

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Since the advent of zeolites in industrial applications, significant efforts have been made to discover mesoporous aluminosilicates. This endeavour aims to enhance the functionality of microporous materials for processing bulky molecules with kinetic diameters that exceed the pore sizes of conventional 12-membered ring (12-MR) zeolites. Although some extra-large pore zeolites have been discovered, only ITQ-37[1] and ITQ-43[2] have demonstrated pore openings reaching the 2 nm threshold, necessary to address the micro/mesoporous gap. Nevertheless, their germanosilicate composition results in poor hydrothermal stability and low aluminum content, restricting their practical applications. Here, we present the first stable meso/microporous aluminosilicate zeolite, ZMQ-1 (Zeolitic Materials, Qingdao Institute of Bioenergy and Bioprocess Technology, No.1)[3,4]. ZMQ-1 features a robust three-dimensional framework with intersecting 28- and 10-membered ring channels, with the 28-MR channel exhibiting a cross-sectional diameter of 22.76 Å × 11.83 Å. This study explores the unique structural and physicochemical characteristics of ZMQ-1, employing techniques such as *in situ* FTIR spectroscopy, solid-state NMR, and argon adsorption. Additionally, its catalytic performance in vacuum gas oil cracking is evaluated and compared to other molecular sieve catalysts, highlighting its potential for industrial applications.

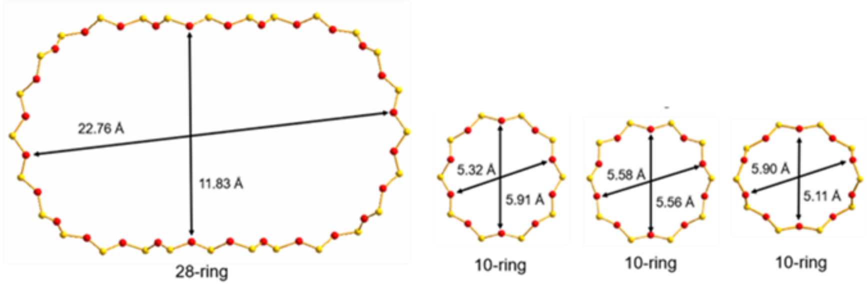

Fig. 1. A schematic depiction of the 28- and 10-membered rings in ZMQ-1, along with their cross-sectional dimensions.

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THEME

X Theme 1 : Synthesis and shaping

☐ Theme 2: Applications for the environment, energy, and health

☐ Theme 3 : Characterization and modeling

Recrystallized micro-mesoporous ferrierite for best biofuel production

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Modifications to zeolite catalysts have allowed to perform in a continuous flow reactor the skeletal isomerization of fatty acid methyl esters (FAME), as required to provide biodiesel with adequate cold-flow properties.[1,2] The reaction is currently carried out in pressurized batch reactors on ferrierite heterogeneous catalysts. The development of continuous flow processes for FAME isomerization on microporous catalysts has been frustrated by fast deactivation, due to passivation of the Brønsted acid asites.

The recrystallization of zeolites in cetyltrimethylammonium (CTA) solution is an accepted method to open a hierarchical micro-mesoporous network and improve the accessibility of the active sites. This treatment has been applied to two kinds of zeolites with different microporosity - 10-member ring (10MR) medium size-micropore ferrierite and 12MR large-micropore high-silica faujasite - producing different structural mesoporosity in the two kinds of zeolites, with formation of MCM-41-like wormlike mesopores in faujasite and opening of a prismatic negative-crystal bottle-neck mesoporosity in ferrierite (Fig. 1).

The latter type of material remarkably improved the stability of the isomerization reactions, with 98 wt% conversion of methyl oleate and 55 % selectivity of branched monoenoic fatty esters upon 8 h time-on-flow, a result uncommon in continuous-flow fatty ester isomerization experiments. The better results obtained on recrystallized ferrierite catalysts are related to the propertiesof both micro- and meso-porosity, through the well-known shape selectivity of the ferrierite structure for alkene isomerization reactions and solvent effect of condensed liquid phase in the bottle-neck mesoporosity. The products of methyl oleate isomerization on ferrierite led to a significant improvement of the cold-flow properties, with freezing points on average 8 °C lower than for faujasite catalysts.

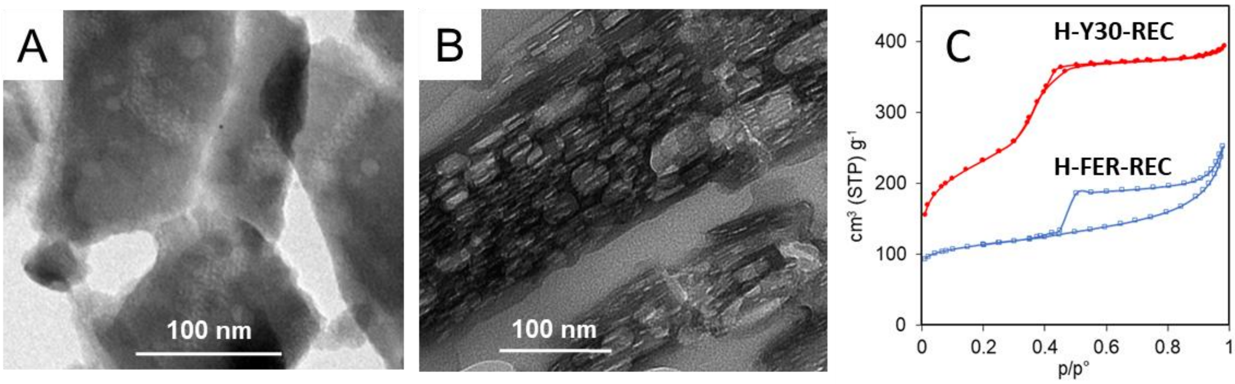

Fig. 1. SEM micrographs of TMA recrystallized faujasite H-Y30-REC (A) and ferrierite H-FRE-REC (B), and N_2 sorption isotherms (B) evidencing the worm-like mesoporosity of H-Y30-REC and the bottom-neck mesoporosity of H-FER-REC.

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THEME

☐ Theme 1 : Synthesis and shaping

☒ Theme 2: Applications for the environment, energy, and health

☐ Theme 3 : Characterization and modeling

Catalytic Potential of Extra-Large Pores ZEO-1 Zeolite

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Introduction

Zeolites are unique crystalline microporous materials used in different industrial applications, such as catalysis and adsorption-separation processes. Their microporous structure is the origin of their shape selectivity, but limits their application for bulkier molecules. Recently, a promising extra-large pore aluminosilicate zeolite, ZEO-1 (JZO), with relatively low Si/Al ratio (~15-20) and high hydrothermal stability, has been prepared [1]. ZEO-1 has a 3D framework with three types of supercages formed by interconnected 16x16, 16x12, and 16x12 member rings (MR) channels. As ZEO-1 is a relatively recent discovery, studies on its catalytic properties remain limited. Since the zeolite was recently discovered and its synthesis is difficult to reproduce, there are a few publications devoted to its catalytic properties [1, 2].

To shed light in ZEO-1's catalytic potential, we investigated its fundamental properties through model reactions: activity was assessed via n-hexane cracking at 540 °C [2], selectivity through phenol alkylation with tert-butyl alcohol at 80 °C [2], and stability via coking reactions with propene at 450 °C. Additionally, spent catalysts were analysed using various methods to identify deactivation modes.

Materials and Method

The materials used in this study include ZEO-1 (16 MR: 10.62 × 9.41 ↔ 10.54 × 9.64; 12 MR: 7.24 × 6.60 ↔ 7.18 × 5.48) and commercial Beta (12 MR: 6.6 x 6.7 ↔ 5.6 x 5.6) and USY (12 MR: 7.4 x 7.4) zeolites. The catalytic tests for n-hexane cracking and propene transformation were conducted in a fixed-bed reactor at 540 °C and 450 °C, respectively, using a nitrogen-to-hydrocarbon molar ratio of 11. The alkylation reaction of phenol with tert-butyl alcohol was performed in the liquid phase using a batch reactor at 80 °C. The spent catalysts obtained after various durations of propene conversion were analyzed to evaluate residual properties.

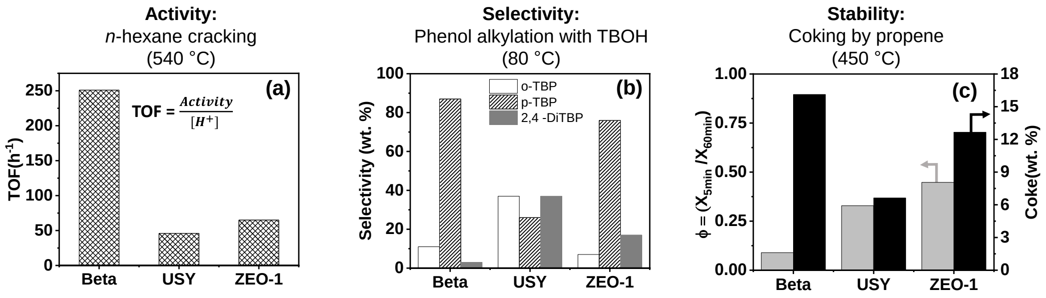

Figure 1. Catalytic activity (a), selectivity (b) and stability (c) of ZEO-1 in comparison with Beta and USY zeolites. Φ: deactivation function, TBOH: tert-butanol, TBP: terbutyl phenol.

Results and Discussion

The strength of Brønsted acid sites was evaluated using the rate of monomolecular cracking of n-hexane, normalized to the concentration of acid sites determined through pyridine adsorption (Figure 1a). The turnover frequency (TOF) results show that ZEO-1 displays slightly greater activity than USY zeolite but significantly lower activity than Beta zeolite. This indicates that ZEO-1 has acid sites with a strength comparable to those of USY.

Phenol alkylation with tert-butyl alcohol is a classic Friedel−Crafts reaction that produces ortho-butyl phenol (o-TBP), para-butyl phenol (p-TBP), and 2,4-di-tert-butyl phenol (2,4-DTBP). The pore size and the channel geometry influence the selectivity for these products [2]. ZEO-1, Beta, and USY achieved phenol conversion rates of 84%, 71%, and 90%, respectively. USY showed minimal product selectivity, yielding similar proportions of o-TBP and 2,4-DTBP, with slightly less p-TBP. In contrast, Beta demonstrated a strong selectivity to p-TBP while producing negligible amounts of o-TBP and 2,4-DTBP. ZEO-1 exhibited a selectivity pattern similar to Beta, favoring p-TBP significantly over the other products (Figure 1b). Although ZEO-1 features a supercage structure with dimensions comparable to USY, its preference for p-TBP over 2,4-DTBP suggests that most active acid sites are located within its 12-MR channels. This conclusion aligns with DFT modeling, which highlights the stability of key tetrahedral sites within these channels [2].

The stability of the catalysts was assessed by monitoring their activity decay during propene transformation (Figure 1c). After 60 minutes of reaction, ZEO-1 maintained a much higher proportion of its initial activity, event after deposition of large amount coke (Figure 1c), compared to Beta and USY, demonstrating its superior stability and resistance to coking. This improved stability is likely due to the limited number of acid sites within ZEO-1's 16-MR channels, which facilitates efficient molecular diffusion. Moreover, the coke molecules formed during propene conversion on ZEO-1 are primarily linear polyaromatics, such as alkyl-naphthalenes and anthracenes, whose sizes match well with its 12-MR channels. In contrast, Beta zeolite and USY produces coke predominantly in the form of alkyl-pyrenes, which become trapped in the channel intersections and cages, accelerating deactivation [3].

Conclusion

The results of the catalytic tests indicate that ZEO-1 zeolite holds significant potential for acid catalysis applications in oil refining, petrochemistry, and sustainable chemistry. Its cracking performance is comparable to that of USY, while its shape selectivity appears to be governed by the 12-MR channels. Furthermore, the 16-MR channels contribute to its enhanced stability, making ZEO-1 a promising candidate for industrial processes that demand efficiency and durability, as well as for advancing greener and more sustainable chemical transformations.

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Enhanced Furfural Conversion into γ-Valerolactone and Isopropyl Levulinate over Catalysts based on Dendritic ZSM-5 Zeolite Modified by ZrO_2 Impregnation

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Lignocellulosic biomass is an abundant and cost-effective resource, making it an attractive option for producing high-value products. In this context, furfural (FFL) can be obtained from hemicellulose hydrolysis in lignocellulosic biomass, which leads to C5 sugars such as xylose. Through a dehydration process, xylose is converted into FFL that represents a promising platform molecule for producing valuable compounds like γ-valerolactone (GVL) [1]. GVL is a highly versatile compound, having a wide range of applications: green solvent, gasoline or fuel additive, and precursor of both biodegradable polymers and sustainable chemicals [2]. Traditionally, Zr−Al-BETA zeolites [1] have been employed in the catalytic conversion of furfural to GVL through Meerwein−Ponndorf−Verley (MPV) reduction, utilizing 2-propanol as a hydrogen donor.

In this work, dendritic ZSM-5 zeolite (d-ZSM-5) with unique trimodal porosity, including zeolitic micropores, mesoporous channels, and meso-macroporous cavities, as well as a high external surface area, has been assessed in FFL conversion assisted by 2-propanol [3]. The catalytic performance of d-ZSM-5 has been compared with that of a nanocrystalline sample (n-ZSM-5) using different ZrO_2 loadings (Fig. 1). The use of the dendritic zeolite supports significantly improved FFL conversion to nearly 92% (compared to 65% obtained using commercial n-ZSM-5) and increased GVL selectivity to c.a 44%, which can be assigned to a higher accessibility and a quite better ZrO_2 dispersion when using the dendritic zeolite regarding the n-ZSM-5 support. Likewise, it promotes the formation of isopropyl levulinate, which is also a valuable product. These results highlight the high potential of dendritic zeolites for the transformation of platform bio-molecules.

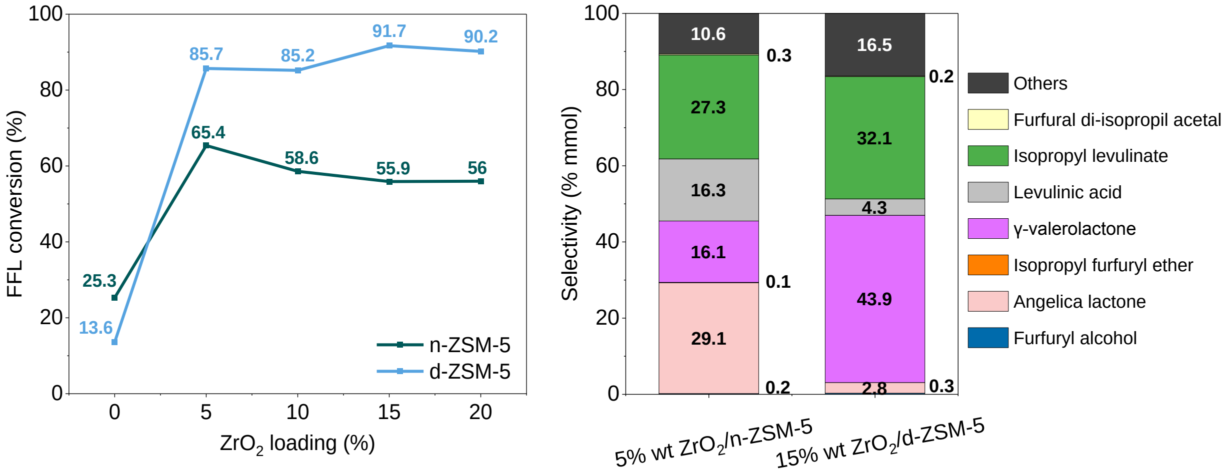

Fig. 1. FFL conversion (a) and product selectivities (b) obtained over n-ZSM-5 y d-ZSM-5 based catalysts. Reaction conditions: 6 h, 180 °C, 30 mL of 2-propanol, $[FFL]_0 = 10\ g\cdot L^{-1}$, catalyst loading 0.1 g.

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THEME

☐ Theme 1: Synthesis and shaping
☒ Theme 2: Applications for the environment, energy, and health
☐ Theme 3: Characterization and modeling

Assessing Zeolites as Catalysts for Biaxially Oriented Polypropylene (BOPP) Chemical Recycling

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Thanks to their remarkable versatility and significant contributions to modern living, plastic materials have become fundamental to daily life. However, their widespread use poses severe environmental challenges, particularly in disposal and recycling. In 2022, Europe produced 58.8 million tons of plastic, but only 26.9% of the 32.3 million tons collected from post-consumer waste was recycled. Mismanagement of around 23.5% of plastic waste highlights the pressing need for enhanced recycling efforts to mitigate environmental harm and move towards a sustainable society. [1, 2]

Plastic waste includes diverse materials, ranging from single-resin plastics with minimal additives to complex multilayered composites like biaxially oriented polypropylene (BOPP). These advanced materials, commonly used in food packaging, offer excellent barrier properties but incorporate additional components, such as silica or alumina, which pose challenges to traditional recycling methods. [3, 4]

Pyrolysis has emerged as a promising alternative for recycling complex plastic waste. Thermal and catalytic pyrolysis, influenced by temperature, polymer type, pressure, and catalyst use, enables plastic conversion into valuable petrochemicals, including fuels. Catalysts play a crucial role by enhancing reaction rates, improving energy efficiency, and optimizing product quality. Catalytic pyrolysis offers significant advantages over thermal methods, demonstrating potential for scalable solutions. [4, 5]

Understanding the pyrolysis process and Thermogravimetric Analysis (TGA) is required to reach robust kinetic data, study plastic degradation's thermal behaviour and kinetics, and design optimally efficient reactor conditions for an effective chemical recycling of BOPP. Research into the pyrolysis kinetics of single-resin plastics has expanded, enabling the development of models to predict reaction behaviour and enhance plastic recycling processes. These advancements underscore the importance of integrating scientific innovation into waste management strategies to address the global plastic crisis. [6]

In this work, the effect of adding HZSM-5 and H-beta zeolites as pyrolysis catalysts was studied and applied to the catalytic degradation of food packaging BOPP films, like chocolate wrap. Although using these catalysts to decompose single-resin plastics is promising, they provided only modest improvements for multi-layered plastics, as Table 1 shows. This communication is intended to discuss the impact of the two catalysts on the kinetics of catalytic pyrolysis and to understand the different behaviour exhibited for BOPP and single resins.

Tab. 1. TGA maximum degradation temperatures (at 10 ºC.min^{-1}) and kinetic parameters for the main component using model fitting models for single resin PP, BOPP films without catalyst and with HZMS-5 and H-beta.

	PP	PP + HZMS-5	PP + H-beta	BOPP	BOPP + HZMS-5	BOPP + H-beta
T max (ºC)	447	397	349	463	470	446
Ea (kJ/mol)	211	129	102	351	341	354
k (s^{-1})	2.31	6.57	11.08	1.85	1.02	6.94

Ea – activation energy, k - rate constant at the reference temperature.

Acknowledgements

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THEME

☐ Theme 1 : Synthesis and shaping
X Theme 2: Applications for the environment, energy, and health
☐ Theme 3 : Characterization and modelling

Injectable chitosan-nanozeolite hydrogels as cation carriers for chronic wounds

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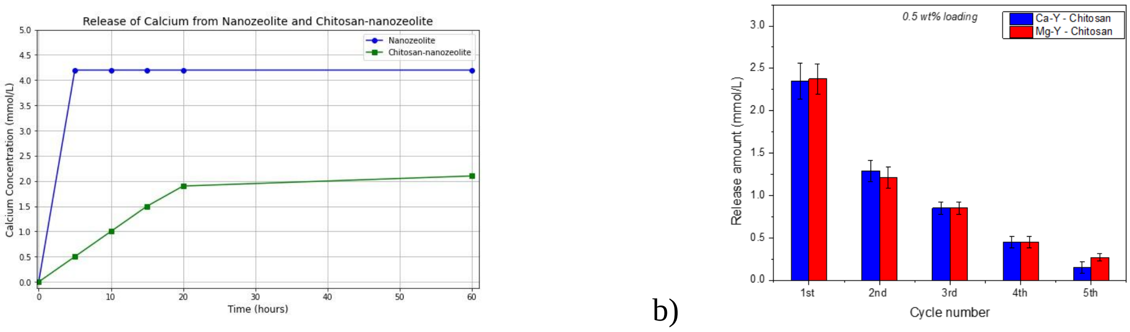
Recent advances in wound healing with cationic salts [1] have highlighted zeolites as promising cation-delivering materials with their unique porosity and cell adhesion properties [2]. However, rapid cation release and particle dispersion require their incorporation in hydrogel matrices which is commonly used in wound healing [3]. The limited availability of such materials and scarcity of detailed investigations on cation release encouraged us to develop an injectable chitosan-nanozeolite hydrogel and examine its cation release behavior.

The hydrogel composite has been prepared by immersing cation-exchanged nanozeolites in chitosan-gluconic acid solution followed by gelation at 37°C. The characterization of nanozeolites confirmed similarity in crystallinity, surface area, and morphology prior to cation exchange while elemental analysis approved the presence of divalent cations in nanozeolites. The release of cations was investigated under two conditions: static, where the medium remained unchanged, and dynamic, where the medium was continuously refreshed. Cation release studies in static condition indicated that hydrogels release 2 times less cation and it reaches its equilibrium slower compared to nanozeolite suspensions (Fig.1.a). Under dynamic conditions, the hydrogel demonstrated the cation release ability for several cycles (Fig.1.b.) and it also revealed the correlation of zeolite loading with released cation concentration. Modelling the release conditions showed that the cation release is due to Fickian diffusion in dynamic conditions whereas it was governed by diffusion and polymer relaxation (non-Fickian diffusion) in static conditions. This controlled release could be linked to the bulky hydrogel matrix and the chelating properties of gluconic acid. Overall, controlled release from nanocomposites make them promising material for targeted cation delivery.



b)

Fig.1. a). The release profiles of cations from chitosan- 0.5wt% nanozeolite hydrogels and nanozeolites in static conditions b). The release of cations from chitosan- 0.5wt% nanozeolite hydrogels in dynamic conditions.

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THEME

☐ Theme 1 : Synthesis and shaping

☒ Theme 2: Applications for the environment, energy, and health

☐ Theme 3 : Characterization and modeling

Roles of cation location in LTA zeolite for methane storage

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Methane storage is achieved by liquefaction (LNG) or compression (CNG) which are poorly energy efficient processes. Adsorbed Natural Gas (ANG) which consists in a reversible storage of methane in microporous solids under more practical conditions of temperature and pressure has recently found applications [1], [2]. The objective of this work is to investigate zeolites which can adsorb methane but hardly desorb it in order to develop a methane storage solution.

From a systematic screening of bicationic **LTA** zeolite, we discovered two specific compositions, namely $K_{4.2}Ca_{3.9}$-LTA and Na11K_1-LTA which show specific methane adsorption-desorption isotherms. Whereas K-LTA and Ca-LTA show no methane adsorption and fully reversible methane adsorption respectively, $K_{4.2}Ca_{3.9}$-LTA and $Na_{11}K_1$-LTA (not shown) show large hysteresis which reflects the possibility of storage (**Fig 1.a**). The hysteresis vanishes when isotherm adsorption temperature increases. Kinetics of desorption were evaluated through manometric and dynamic home-made chromatographic experiments. Results indicate that methane can be strongly trapped in specific zeolites, i.e. very minor desorption occurs at normal P and T.

Surprisingly, Rietveld refinement shows that the unit cell of $K_{4.2}Ca_{3.9}A$ is not intermediate with respect to the monocationic zeolites Ca-LTA and K-LTA (**Fig 1.b**). Also, we can observe an increase of the cell volume of $K_{4.2}Ca_{3.9}A$ when the temperature increase. We propose a temperature-dependent "gate-opening" mechanism which would be triggered by the mobility of K^+ between site I and II.

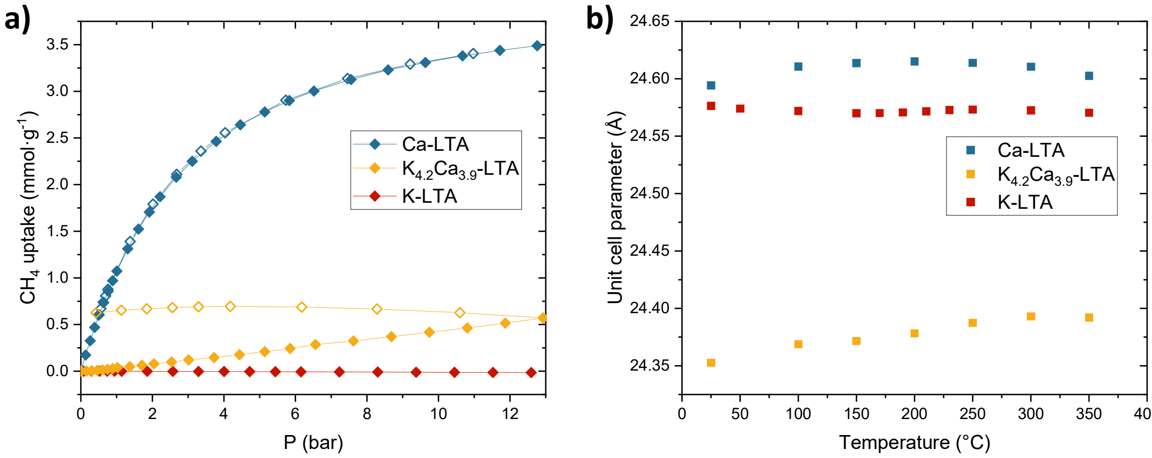

Fig. 1. a) Adsorption isotherms on K-LTA, Ca-LTA and $K_{4.2}Ca_{3.9}$-LTA zeolites at 298 K; **b)** Thermal evolution of the unit cell parameters of those dehydrated zeolites.

This study demonstrates the significant potential of specifically tailored zeolites for gas storage at ambient pressure and temperature, achieving a storage density of methane that is twenty times greater than its natural density for the same P and T conditions. We assume that the underlying "gate-opening" mechanism is linked to the cation mobility triggered by the temperature.

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THEME

☐ Theme 1 : Synthesis and shaping

☒ Theme 2: Applications for the environment, energy, and health

☐ Theme 3 : Characterization and modeling

Acid gas valorisation on Na-Faujasite: catalytic COS formation

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Background and motivation. Refineries and petrochemical industries manage over 3.6 million tons (Mt) of hydrogen sulphide (H_2S) each year [1], mixed with CO_2 as acid gas, which is encountered in refining, exploration and production, and in biogas treatment, etc. Existing technologies do not enable the simultaneous reduction of CO_2 and H_2S. The project eCODUCT introduces an innovative two-step technology for acid gas valorisation: i) conversion of CO_2 and H_2S into carbonyl sulphide (COS) in a fixed-bed reactor via the reaction: $H_2S(g) + CO_2(g) \rightleftharpoons COS(g) + H_2O(ads)$. ii) COS conversion into carbon monoxide (CO) and elemental sulphur (S_x) using an electrothermal fluidized bed (ETFB) reactor.

In this work, we address the first step (i) by studying the role of FAU-type basic zeolites on the competitive desorption and reaction of CO_2 and H_2S supported by the development of a microkinetic model.

Materials and methods. Adsorption and reaction of CO_2 and H_2S were performed at atmospheric pressure in a fixed-bed quartz reactor at variable temperatures from 45 to 120°C. All samples were pre-treated at 350°C under nitrogen flow 1.8 L/H (STP) for 8-10 h before being fed with the acid gas mixture with different flow sequences.

Results and discussion. The amount of H_2S and CO_2 adsorbed individually on 13X zeolite is less than 10%, corresponding to a very low ratio relative to the sodium cation (0.6 mol/g for 13X). The overall interaction strength of H_2S with the adsorption site is greater than CO_2, likely due to a dissociative adsorption mechanism on the sodium cation [2]. A series of experiments was conducted on 13X zeolite samples pre-saturated with H_2S to investigate the kinetics of COS formation (Fig. 1). Chemisorbed H_2S is completely converted upon reaction with CO_2. COS production profile passes through a maximum and then decreases with the reaction time, evidencing the progressive deactivation of the catalyst. Temperature significantly influenced the reaction, where the highest COS yield was observed at 100°C. The experimental data were used to develop a microkinetic model based on the Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetics. This model successfully describes the concentration variation of both reagents and products during the reaction on pre-saturated samples, and considers water, reaction co-product, as the primary factor driving catalyst deactivation over time.

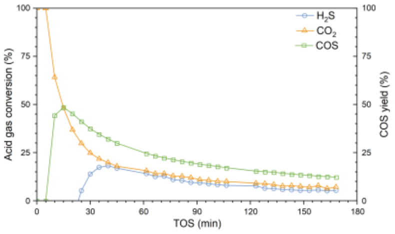

Fig. 1. Conversion of H_2S, CO_2 (left axis) and yield of COS (right axis) vs. time on 13X zeolite at 100°C.

Acknowledgments. https://e-coduct.eu, Horizon Europe Grant Agreement n. 101058100.

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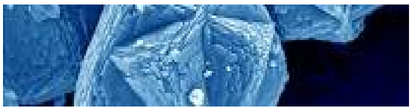

THEME

☐ Theme 1 : Synthesis and shaping

☒ Theme 2: Applications for the environment, energy, and health

☐ Theme 3 : Characterization and modeling

How is the promoter influencing the stability of Ni based catalyst for dry reforming of methane?

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The utilisation of CO_2 is in focus of research studies and industry, in order to offer alternatives for the obtention of energy products and fuels. Dry reforming of methane (DRM) process is proposing the use of CO_2 feedstock for the production of hydrogen rich gas [1]. It is well known that Ni based catalyst results in good catalytic in DRM reaction [2,3]. Nevertheless, their performances in DRM, can be improved by playing on the design of a catalyst with accurate control of the active site surface and the nature of their local environment.

In this regard, we study here, the influence of the support chemistry over DRM reaction, for highly dispersed Ni NPs (10 wt.%) based catalyst. A hybrid support h-SBA-15 (h=Al, Ce, and Zr) with highly dispersed h-elements obtained by adapted methods is used. Metallic Ni is obtained by the H_2 reduction of the materials synthetized by micro-melt infiltration route. All the solids obtained were characterized by: XRD, in situ-XRD, N_2 physisorption, H_2-TPR, in situ-XPS, S/TEM-EDXS-EELS in order to evaluate the material morphology, structure, reducibility and stability. The evaluation of the DRM performances is done in the following conditions: m_{cat}=100 mg, T_{red} = 600 °C and T_{DRM} = 700 °C (red), 1 atm, CH_4/CO_2 = 1, CH_4 and CO_2 at 20 vol.%, 30,000 mL $gcat^{-1}h^{-1}$.

First, the support characterization was done in order to proof the well incorporation of the additional element. The morphology is showing that the structure is well maintained for Zr and Ce, while Al is exposing partial destruction of the support. For all the Ni supported catalysts, Ni NPs are of sizes below 3 nm, having high dispersion onto the hybrid h-SBA-15 support as showed by, XRD and S/TEM-EDXS images (Fig. 1). The reducibility was evaluated by H_2-TPR, and the reduction profiles are confirming the presence of small NiO NPs, that are reduced at T_{max} of ~ 550 °C, while T= 600 °C is suggesting the possible interaction with the support.

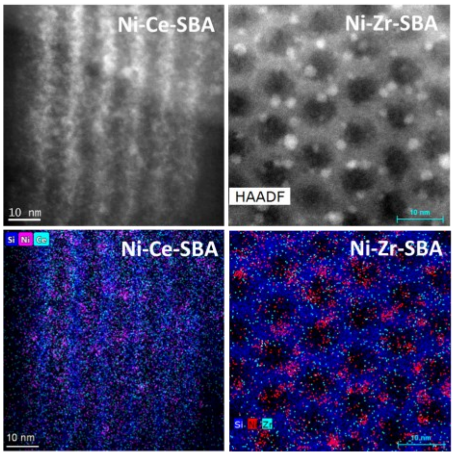

Fig. 1. HAADF-STEM-EDXS mapping for Ni supported on hybrid-SBA supports

The characterizations realized for reduced solids at T= 700 °C and are showing that metallic Ni NPs are maintaining a low size after reduction in such conditions. The evaluation under DRM, is showing by far best performances for Ni-Zr-SBA, with 78 % (CO_2) and 70 % (CH_4) and a high stability after 80 h of test, with remarkable carbon resistance comparing to monometallic Ni.

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THEME

☐ Theme 1 : Synthesis and shaping
☒ Theme 2: Applications for the environment, energy, and health
☐ Theme 3 : Characterization and modelling

How to enhance a catalytic reaction process by using zeolite and MOFs as sorbents?

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Methanol is one of the most widely used chemicals, being employed both as a platform in the chemical industry and as a sustainable fuel in the context of the energy transition. Its synthesis from syngas has been well-established for a long time. However, there is still a considerable room for improvement due to the low conversions caused by thermodynamic limitations. To overcome the latter thermodynamic issues, more complex processes than conventional catalytic fixed bed reactors must be developed [1-2]. In this context, Sorption Enhanced Reaction Process (SERP) is a cyclic technology where water by-product is removed, thanks to sorbents, to shift the reaction equilibrium toward products formation [3-4], according to Le Chatelier principle.

This study presents SERPs in a wide range of pressure and temperature, using pure CO_2 and simulated recycled feeds for several sorbents. The reaction conditions are relevant to the industrial one and special attention is paid to the sorbents. Figure 1 shows a comparison between a conventional fixed bed reactor and SERP under the same conditions: the sorbent adsorbs a part of the water, represented by diagonal stripes, which allows yielding an overshoot (vertical stripes) during the transient regime. At this time, the thermodynamic limits of the catalyst-only system have been outperformed. Then the sorbent is saturated with water and therefore inactive; the system behaves therefore like conventional fixed bed reactor containing only the catalyst (CZA).

This work is focused on 13X zeolite, MIL-120 and CAU-10 MOFs as sorbents in different conditions of feed, pressure and temperature. The novelty of this work relies on the originality and diversity of the sorbents, the wide range of reaction conditions, and the analytical setup that allows a complete understanding of the system.

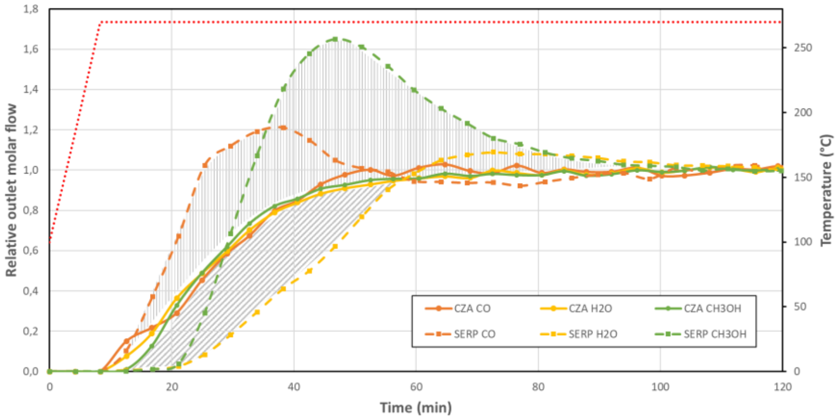

Figure 1: Relative outlet molar flow of CO, H_2O and CH_3OH for CZA-SiC (CZA) and CZA-13X (SERP). T = 270°C, P = 50 bar, H_2/CO_2 ratio = 3, catalyst/sorbent ratio = 0.125, $W_{catalyst} / F = 0.3$ g s/cm^3.

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THEME

☐ Theme 3 : Characterization and modeling

Evaluating the influence of stream contaminants on the carbon capture potential of prototypical porous materials

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Solid sorbents such as zeolites, MOFs, and finely divided metal oxides are one of the most promising candidates for the implementation of carbon capture, both for direct air capture (DAC) solutions and point sources (PS). Bringing a promising material from the lab to industry requires a realistic evaluation of its performance in process relevant conditions. The main goal from a materials standpoint is identifying and screening sorbents with the necessary affinity at the relevant CO_2 concentration (from 400 ppm up to 100%), long term usability, regeneration conditions, and thermal properties[1].

One of the most pertinent challenges relies in the presence of minor contaminants in the process stream, such as H_2O (for DAC and PS) of SO_x/NO_x/sour gas (for PS) and atmospheric volatile organic compounds (for DAC). All contaminants can compete with CO_2 for sorption sites. In some sorbents, the presence of a certain amount of humidity can increase total amount adsorbed, or speed up the sorption kinetics, as in the case of amine-based materials[2] and alkali or alkaline earth metal carbonation processes.[3] Finally, even small concentrations (ppm) of noxious gas may poison and degrade sorbents.

Therefore, assessing the influence of contaminants on the CO_2 uptake is of crucial importance. In this work we explore several methods of accomplishing this task – gravimetry and micro-breakthrough analysis – and then walk through several examples on three commercially available prototypical materials – Zeolite 13X, CALF-20, and Lewatit VP OC 1065.

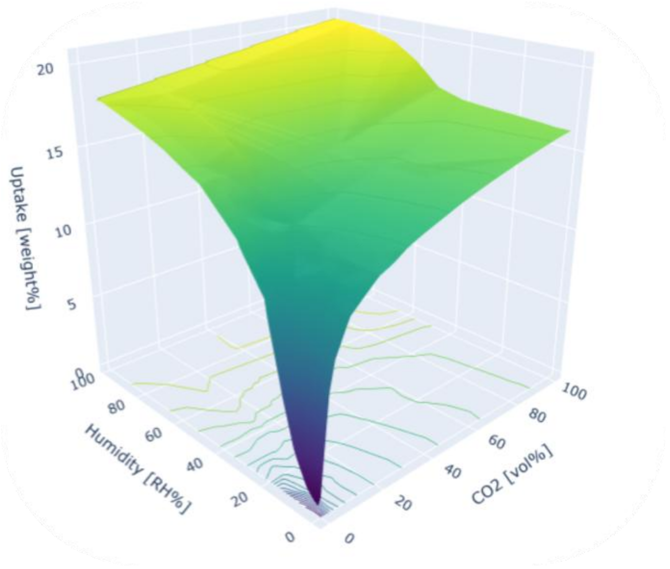

Fig. 1. Sorption capacity surface for CALF-20 at 25 °C including water, CO_2 and co-sorption concentrations.

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THEME

☐ Theme 1 : Synthesis and shaping

☐ Theme 2: Applications for the environment, energy, and health

☒ Theme 3 : Characterization and modelling

From Solid Precursors to Zeolite-Templated Carbon: A Molecular Odyssey Toward Porous Carbon Frameworks

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Zeolite-Templated Carbons (ZTCs) constitute an advanced class of nanostructured, highly porous carbon materials formed through a negative replication process of zeolite frameworks using diverse carbon precursors [1]. Recently, a solid-state route employing anthracene as the carbon source has been developed, enabling the synthesis of ZTCs with distinctive structural features [2]. Beyond these advances, there is substantial scope for tailoring ZTC properties, ranging from heteroatom incorporation to controlled structural characteristics.

In this study, we deepen the mechanistic understanding of solid-state ZTC synthesis by examining the structural and chemical evolution of impregnated protonic Y zeolite using three newly selected molecular precursors: *trans*-stilbene (t-St), *para*-terphenyl (PTP), and phenothiazine (PTZ). By Electron Paramagnetic Resonance (EPR) measurements, we uncovered the temperature-dependent dynamics of radical species formation within the zeolite, thereby revealing the influence of molecular reactivity and radical intermediates (Figure 1). Coupling these insights with a suite of complementary analytical techniques: UV/Vis spectroscopy, Raman spectroscopy, nitrogen physisorption at 77 K, X-ray diffraction, and electron microscopy, allowed us to visualize the molecular-to-material transformation pathways.

Our findings reveal that the molecular structure of the precursor exerts an influence on the emerging carbon structural and textural properties. By establishing this mechanistic foundation for solid-state ZTC synthesis, our work provides a versatile template for the design of microporous carbon materials.

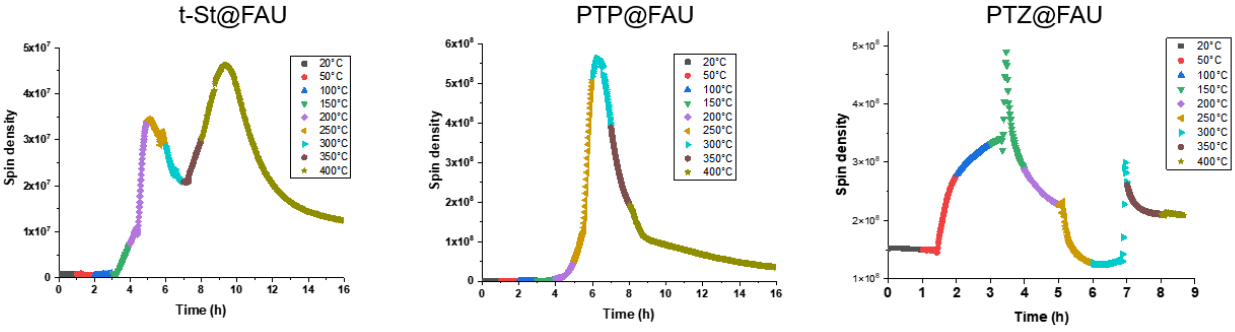

Fig. 1. First step of ZTC formation: evolution of radical formation in (a) trans-stilbene, (b) para-terphenyl, and (c) phenothiazine incorporated into FAU framework, monitored by EPR spectroscopy across the temperature range from ambient to 400 °C.

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THEME

☐ Theme 1 : Synthesis and shaping
☐ Theme 2: Applications for the environment, energy, and health
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Zeolite's positive role in platinum-catalyzed hydrogenation: Evidence from high-throughput infrared studies

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The hydrogenation of unsaturated molecules is a critical industrial reaction, with catalyst performance influenced by both metallic active sites and support materials[1,2]. This study explores the role of Pt/SiO_2 and ZSM-5 (Si/Al = 11) zeolite mixtures in pyridine hydrogenation, using high-throughput infrared spectroscopy to analyse kinetics under varying hydrogen pressures. Conducted at 110°C in a "Caroucell" infrared cell[3], the experiments investigated zeolite proportions of 25%, 50%, and 75%.

The results revealed that hydrogen pressure plays a pivotal role in hydrogenation efficiency. At low pressure (15 Torr), the conversion of pyridine to piperidine (band at 1473 cm^{-1}) was slow, particularly in a 1:1 Pt/SiO_2-ZSM-5 mixture (figure 1a). However, increasing the hydrogen pressure significantly enhanced conversion, indicating that elevated pressures promote the diffusion of activated hydrogen species (H_{SP}). Zeolite in the catalyst mixtures further improved hydrogen adsorption through the spillover mechanism, which is crucial for transferring activated hydrogen to reaction sites. Additionally, surface diffusion contributed notably to the conversion of adsorbed pyridine, with its impact increasing alongside hydrogen pressure. As depicted in (figure 1b), the first-order reaction kinetics reveal that the optimal reaction rate constant was achieved with the 25% zeolite mixture. This finding indicates that the reaction rate constant (k) is directly influenced by the diffusion time (DT), the time for the first piperidine bands to appear at low pressure, ranging from 100 to 600 min. Notably, the Diffusion Time of Hsp traveling from the Pt/SiO_2 to the zeolite increases with higher zeolite content in the mixture (figure 1c). Therefore pyridine, plays a dual role in this system—not only as a reactant but also as an active participant driving the spillover process. Acting as a "pumping machine," pyridine facilitates the transfer of hydrogen species across the catalyst, ensuring effective interaction with Brønsted acid sites within the zeolite[2].

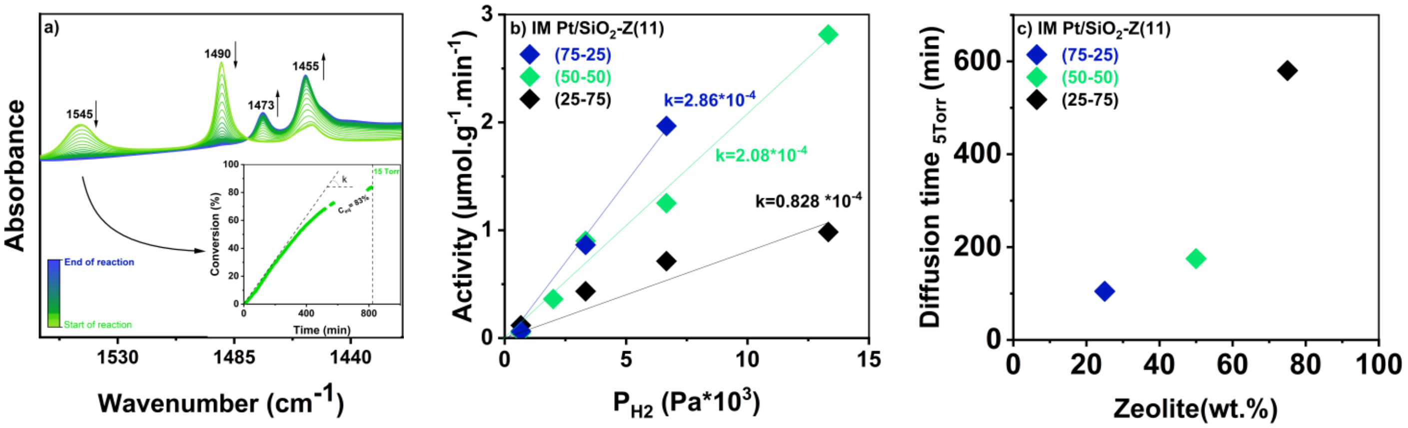

Fig. 1. a) Tracking Reaction Dynamics: Analysis of 1000 Infrared Spectra Over 15 Hours at 15 Torr and Conversion vs. time b) Catalyst Activity vs. Hydrogen Pressure c) DT vs zeolite content

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THEME

☐ Theme 1 : Synthesis and shaping
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Cation-Exchanged LTA Zeolites for Propane / Propylene Separation

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The separation of propane and propylene represents one of the most energy-intensive separations in chemical industry. As an alternative to cryogenic distillation, adsorption using microporous zeolites might offer an alternative. LTA zeolites have been shown to be promising adsorbents, but a systematic study of the effect of the extra-framework cations on propylene and propane adsorption is lacking.

In this work, we synthesized LTA zeolites exchanged with different cations (Na^+, Li^+, Ca^{2+}, Mg^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+}). All exchanged samples were synthesized with Na+ as counterion and then partially exchanged with the other cation (30% and 50%). A comparison was made with pure Si-LTA. Adsorption isotherms were measured using a manometric system, coupled to a Tian-Calvet calorimeter, allowing the simultaneous measurement of the adsorption pseudo-differential enthalpy. While Si-LTA shows no preferential adsorption of propane or propylene and is essentially homogeneous for both probe molecules, propylene shows a strong interaction with divalent cations (Mn^{2+} / Zn^{2+} / Ca^{2+} / Mg^{2+}). For cations with a weaker interaction Ca^{2+} / Mg^{2+}, the energy profile follows the 'classical' shape of an energetically heterogeneous adsorbent. For Mn^{2+} and Zn^{2+}, a distinct step can be observed in the propylene isotherm, together with 2 distinct steps in the adsorption enthalpy profile. On the other hand, LTA zeolites with monovalent cations (Na+ / Li+) show slow diffusion of propane, opening perspectives for a kinetic separation.[1]

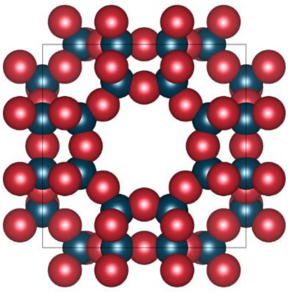

Figure 1. View along the LTA pore opening.

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THEME Theme 3 : Characterization and modeling

Isobutanol to linear butenes: Unravelling competing catalytic reactions sharing a common transition state though Blue moon sampling

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The dehydration of bio-based butanols to butenes catalyzed by acidic zeolites is a key step in sustainable hydrocarbon production. Experimental studies have revealed a high selectivity for conversion of isobutanol to linear butenes[1,2], and despite high technological potential, the mechanisms of these transformations are not yet fully understood. Our previous static theoretical work[3] therefore represents the first systematic effort to explore possible routes linking isobutanol to all butene products. While the static approach, based on statistical mechanics approximation, is useful for qualitative analysis, its accuracy is insufficient for realistic predictions[4] of rate constants. To address this, we employed Blue moon ensemble[5] *ab initio* molecular dynamics (AIMD) at 100 K and 500 K with a path-based reaction coordinate[6] and Bennett-Chandler theory to study the key reaction mechanisms of isobutanol to butene transformations in zeolite chabazite (periodic DFT calculations were performed in VASP with PBE functional and D2 correction to dispersion interactions)

In addition to the key step of the dominant pathway leading from isobutanol to linear butenes (green path in Fig. 1), its competing pathway for direct isobutanol to linear butene transformation (blue path in Fig. 1) has been studied in the present work[7]. AIMD revealed that these two reactions share common dynamical transition state, with product formation determined by fine details, such as specific atomic positions and momenta that are subject to essentially random fluctuations during the diffusive motion of water. Since the transition state theory is unable to determine the relative importance of these pathways, Bennett-Chandler theory was used to calculate relative transmission coefficients. It was found that from 100 K to 500 K, the preference for isomerization (two step pathway) decreases and the preference for synchronous dehydration and isomerization (one step pathway) increases.

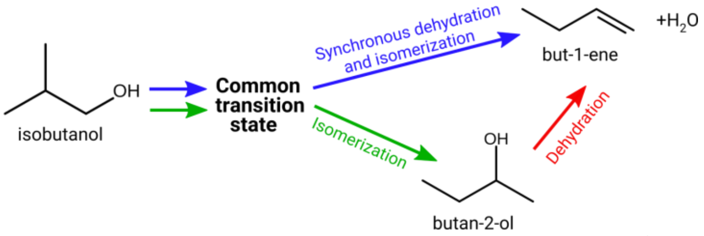

Fig. 1. Competing reaction pathways proceeding via a common transition state for transformation of isobutanol to but-1-ene.

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THEME

☐ Theme 1: Synthesis and shaping
☐ Theme 2: Applications for the environment, energy, and health
☒ Theme 3: Characterization and modeling

New synthesis route for Y/ZSM-5 zeolites: Validated through model reactions

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The industrial FCC catalysts are prepared by synthesizing two zeolites separately, modifying them through post-treatment, and subsequently mixing them to enhance catalytic performance. [1,2] This work reports the preparation of zeolite composite composed of hierarchical zeolite Y and nano-sized ZSM-5 zeolite by quasi in-situ interzeolite conversion approach. Further, the samples were evaluated using two model reactions: methanol-to-olefins (MTO) and n-hexane cracking (developed later).

The protocol for preparing the Y/ZSM-5 compound is described below. A reference mechanical mixture (MM) was made with similar properties to the composite. MTO tests were conducted at 450°C with WHSV 2.1 $g_{MeOH}\ g_{cat}^{-1}\ h^{-1}$.

$$\text{USY} \xrightarrow{\text{Dealumination}} \text{USY-A} \xrightarrow[\text{Recrystallisation}]{\text{Dissolution}} \text{Y/ZSM-5}$$

Figure 1 shows methanol (MeOH) and diemthylether (DME) conversion as a function of time-on stream (TOS) and product selectivity and ethene/propene ratio at 12-30% iso-conversion during deactivation regime of USY, USY-A, Y/ZSM-5 and MM.

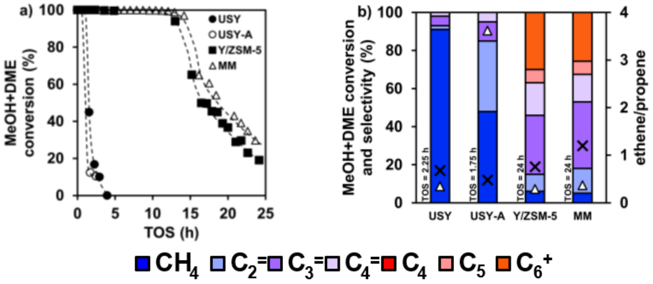

Fig. 1. a) MeOH and DME conversion over TOS, cumulative products selectivity and ethene/propene ratio at b) 12-30% iso-conversion deactivation conditions. White triangles (=ethene/propene ratios); black crosses (=conversions).

The deactivation patterns show a typical deactivation mode for FAU type zeolites. Coke precursor species retained in the zeolite structure could react with methanol, resulting in a dominant dehydrogenation reaction with methane as hydrogen-rich co-product. [3] The Y/ZSM-5 composite shows improved stability with a protective effect originated by the presence of ZSM-5 crystals on the USY-A zeolite. MM catalyst, showing similar results to those of the composite material, confirms its expected composition.

The Y/ZSM-5 interzeolite conversion synthesis overcomes limitations of traditional methods. The composite's stability underscores its potential for advanced catalysis. This method opens pathways for next-generation zeolites in catalysis, adsorption, and separation.

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THEME

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Ultrafast Femtosecond Laser Spectroscopy Of Heterogeneous Solid Photoactive Catalysts For The Conversion Of Methane

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Abstract

The photoconversion of methane into valuable chemicals is pivotal for advancing sustainable chemical processes and vaporizing abundant methane greenhouse gas. Femtosecond time-resolved UV pump-IR probe spectroscopy was employed to investigate the influence of Pt concentration on free electron lifetimes and recombination dynamics in TiO_2-based photocatalysts modified with heteropolyanion layers and anchored Pt atoms (Pt-NPW-TiO_2) [1]. We characterized the charge recombination dynamics dependence on the excitation intensity, by performing the measurements within a low intensity regime ($I_0 \leq 0.05$ mJ/cm²) we isolate the effects of Pt concentration on the kinetics. At low Pt loadings (<1 wt%), dispersed Pt atoms exhibit negligible impact on sub-nanosecond electron lifetimes. However, at higher Pt content (5 wt%), the survival probability of electrons increases significantly, likely due to enhanced charge separation facilitated by chemical modifications in the catalyst, such as altered diffusion rates, activation energy, or Pt nanoparticle formation. This study provides valuable insights into optimizing methane photoconversion efficiency, contributing to advancements in porous materials and photocatalysis. By shedding light on how metal composition affects charge dynamics, these findings establish a strategic framework for the rational design of TiO_2-based photocatalysts or metal oxide-zeolites composites.

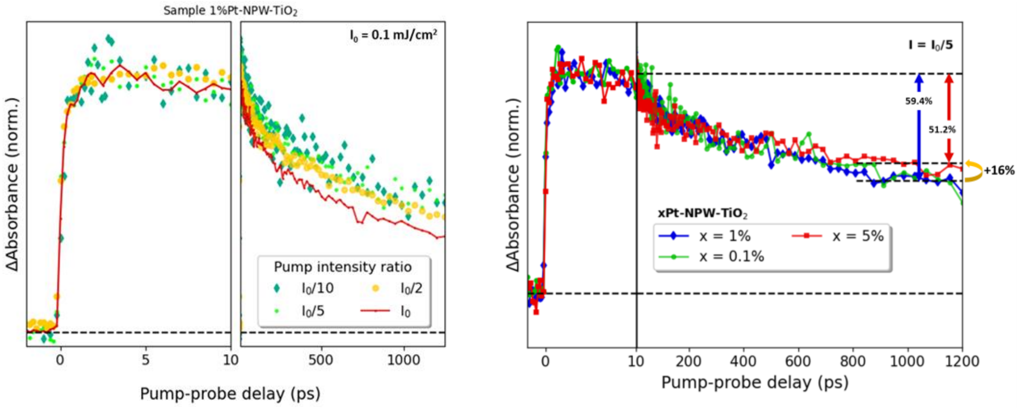

Fig. 1. (a) Kinetic traces for 1%Pt-NPW-TiO_2 with $I_0/10 \leq I_{pump} \leq I_0$. **(b)** Kinetic traces at $I_{pump} = I_0/5$ (linear regime), for xPt-NPW-TiO_2 (x= 0.1, 1, 5 wt%).

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POSTERS
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☒ Theme 1 : Synthesis and shaping

☐ Theme 2: Applications for the environment, energy, and health

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Hydrodesulfurization of Thiophene over Ni doped MoS_2 -supported mesoporous silica

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Hydrodesulfurization (HDS) is a critical process in the petroleum industry for removing sulfur compounds from fuels, ensuring compliance with stringent environmental regulations. The development of high-performance HDS catalysts is essential for improving sulfur removal efficiency. Molybdenum disulfide (MoS_2) is widely recognized for its excellent catalytic activity and sulfur resistance, making it a suitable candidate as the active component in HDS reactions. To further enhance its catalytic performance, mesoporous silica, such as SBA-15, is considered to be used as a support material. SBA-15 is selected due to its high surface area, uniform pore structure, and thermal stability, which facilitate efficient metal dispersion and maximize the accessibility of active sites on MoS_2. Herein, we report the synthesis of nickel-doped MoS_2 supported on SBA-15 using a one-step hydrothermal approach. The resulting material was subjected to calcination at 550 °C, followed by in-situ sulfidation under 10% H_2S/H_2 atmosphere at temperature of 350 °C.
The Raman spectra of SBA-15@MoS_2 and SBA-15@Ni-MoS_2 display two characteristic vibrational modes of MoS_2 : the in-plane mode at 378 cm^{-1} ($E_{1}^{2\,g}$) and the out-of-plane mode at 404 cm^{-1} ($A_{1\,g}$), confirming the successful synthesis of 2H-MoS_2 . Moreover, SBA-15@Ni-MoS_2 exhibits a distinct vibrational peak at 297 cm^{-1} (E_g), attributed to the NiS_2 phase. Small-angle XRD and HAADF-STEM characterizations further reveal the formation of well-defined ordered mesoporous silica.
The mesoporous SBA-15@Ni-MoS_2 demonstrated good HDS performance, achieving a thiophene HDS rate of 8 $mol\cdot h^{-1}\cdot kg^{-1}$ at temperature of 350 °C. This performance significantly higher than SBA-15@MoS_2 (3.5 $mol\cdot h^{-1}\cdot kg^{-1}$) and unsupported MoS_2 (0.27 $mol\cdot h^{-1}\cdot kg^{-1}$). The introduction of Ni as a promoter creates defects and structural disorder within the MoS_2 lattice, promoting the formation of non-stoichiometric, highly active MoS_2 species, which are crucial for enhancing catalytic performance in HDS reactions.

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THEME

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Face-directed assembly of tailored isoreticular MOFs using centring structure-directing agents[1]

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Controlling the design of porous architectures in three dimensions is a fundamental challenge to develop finely-tuned sorbents that meet the needs of a fast evolving and actual high energy consuming society. Molecular building blocks with low connectivity are prone to polymorphism, demonstrated by the vast diversity of 4-connected zeolitic nets (>250), and represents an obstacle for the practice of isoreticular chemistry. This work describes how polytopic expanding and/or tightening binding structure directing agents (SDAs) can be identified, selected and used to alter and control the inclination of adjacent supermolecular building blocks. Zeoliticmetal-organic frameworks (ZMOFs) platform that deviate from the default mtn topology and adopt an underlying sodalite (sod) network is suitable for the rational assembly of multinary materials. In addition to the wide variety of metal cations (In, Fe, Co, Ni), diverse SDAs (di-, tri-, tetra-, hexa-; pyridyl or imidazole) are employed, and combined. The versatility of this approach enables possibilities at both extremities of the porous materials spectrum: From the small ZMOFs with small aperture window for efficient gas separation to the wide mesoporous ZMOFs for gas storage.

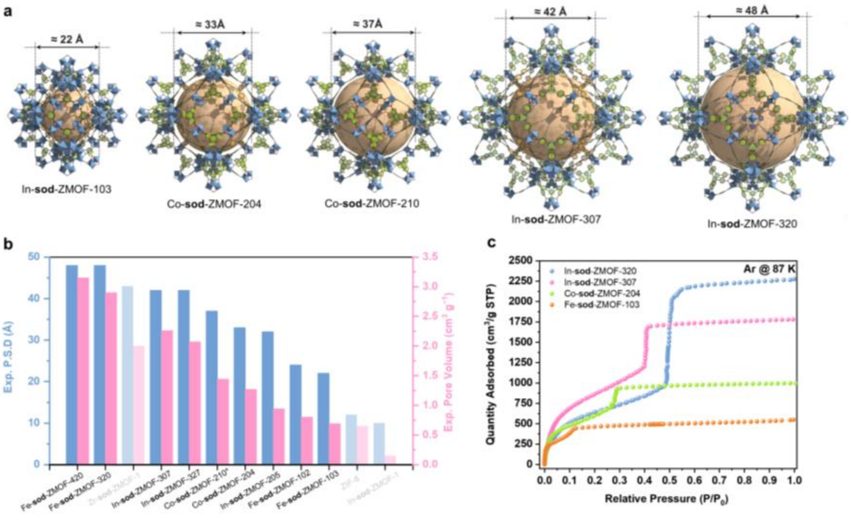

Figure. (a) Range of sod-ZMOF β-cages and data sizes estimation from SCXRD in angstroms (b) Comparison between sod-ZMOFs reported in the paper and other sod-ZMOFs (shown in pale). Experimental total pore volumes calculated from Ar 87K sorption isotherms are shown with pink rectangles; * - calculated from N_2 77K sorption isotherm; pore size distributions (PSD) average size for each ZMOF calculated from Ar 87K sorption isotherms are shown with blue rectangles. (c) Ar 87K sorption curves for different sod-ZMOFs.

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THEME

☒ Theme 1 : Synthesis and shaping

☐ Theme 2: Applications for the environment, energy, and health

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One-pot synthesis of Faujasite from natural clay via high pressure hydrothermal method

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Zeolites are widely used as catalysts, ion exchangers and adsorbents in many separation processes. The synthesis of zeolites is usually performed following the hydrothermal method by using various chemicals (sources of Si and Al, structure directing agent, etc.). The aim of this study is to propose a one-pot synthesis of faujasite (FAU X) by using natural clays, as sources of Si and Al, and water under high pressure as a solvent. Kaolinite was used as the main source of Si and Al and was first transformed into metakaolinite (amorphous product) via thermal treatment. Sources of Si and sodium hydroxide were added to respectively adjust the Si/Al ratio and the charge compensation. For this high pressure (hp-) hydrothermal method, all reactants are placed in a closed vessel with water as solvent and to control the pressure (1 kbar H_2O pressure) [1, 2]. The influence of different factors affecting the nature of the reaction products has been investigated (temperature, time, pressure, Si/Al ratio and amount of alkali). Well-crystallized FAU X was successfully synthesized at low temperature (below 110 °C) with high purity as shown by XRD and N_2 adsorption at 77K. Characterization by SEM revealed the formation of well-defined octahedral crystals indicative of the uniform morphology characteristic of FAU X (Figure 1). These results showcase the hp hydrothermal synthesis method as an effective and simple approach for producing high-quality faujasite with tunable attributes which will hereafter be used for the removal of highly toxic halogenated compounds from both liquid and gas phase.

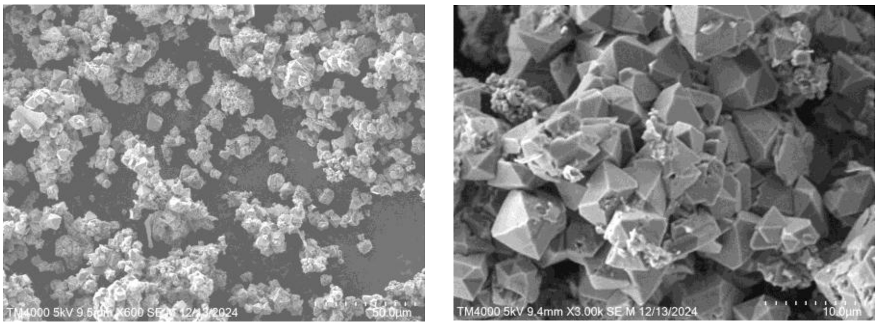

Figure 1: SEM images of synthesized FAU X

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THEME

☒ Theme 1 : Synthesis and shaping

☐ Theme 2: Applications for the environment, energy, and health

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Shaped copper and cobalt-based MOFs decorated with graphene oxide: composites with improved hydrolytic stability and enhanced CO_2 adsorption

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Metal-Organic Frameworks (MOFs) are highly porous and crystalline materials that have garnered interest in fields like catalysis, energy storage, and gas sorption since their emergence in the 2000s. However, their industrial application has been limited by processing challenges and low chemical and thermal stability [1]. To mitigate issues like porosity loss and crystallinity damage from physical shaping methods, researchers propose using chemical shaping through the integration of MOFs with biopolymers such as chitosan (CS) and alginate (Alg). This approach allows for the creation of various shaped composite materials while maintaining the properties of MOFs [2].

Typically, shaping MOFs through combination with a polymer occurs using either *in-situ* or *ex-situ* growth (direct mixing) strategies. However, the simplicity, uniform distribution of MOFs within the polymer matrix, and enhanced interactions between the polymer and MOFs often favor the *in-situ* method over the *ex-situ* approach. In our works, we examined the effects of chitosan and alginate biopolymers on the textural properties of HKUST-1, shaped into CS@HKUST-1 and Alg@HKUST-1 beads through an *in-situ* growth strategy under mild conditions. The results reveal that the chitosan matrix is more suitable for growing HKUST-1 crystals at room temperature, leading to composite beads with specific surface areas (S_{BET}) up to 923 $m^2.g^{-1}$. To address the weak water stability of HKUST-1, graphene oxide was blended with chitosan and the MOF precursors, resulting in ternary composite beads (Fig. 1.b) with high crystallinity and porosity (879 $m^2.g^{-1}$), and improved structural stability in water (up to 48 hours, compared to less than 24 hours for the pristine MOF) [3]. Furthermore, to assess the viability of this approach, we also developed CS@CPO-27-Co binary and ternary composites, resulting in robust beads with high crystallinity and specific surface areas exceeding 500 $m^2.g^{-1}$ [4]. The as prepared CS@HKUST-1 and CS@CPO-27-Co (Fig.1.a.b) were tested for the CO_2 capture, were they showed adsorption capacities of 2.60 and 3.10 $mmol.g^{-1}$, respectively at 298 K.

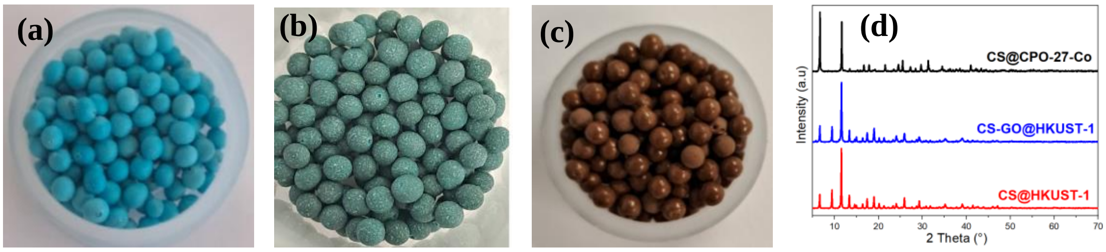

Fig. 1. The as-prepared CS@HKUST-1 (a), CS-Go@HKUST-1 (b), and CS@CPO-27-Co (c) beads, and their corresponding PXRD patterns (d).

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THEME

☒ Theme 1 : Synthesis and shaping
☐ Theme 2: Applications for the environment, energy, and health
☐ Theme 3 : Characterization and modeling

Lanthanide Metal-Organic Frameworks prepared in deep eutectic solvents

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Metal-organic frameworks (MOFs), known for their excellent gas sorption properties, have been widely explored, explaining the existence in the literature of multiple synthesis pathways [1]. One less studied approach is the use of deep eutectic solvents (DESs). DESs are mixtures of at least two components which, at the eutectic ratio, feature a depression of the melting point [2]. These solvents, known to be biodegradable and less toxic, permit to avoid using toxic flammable solvents like DMF, commonly used to synthesize those interesting materials.

In this study, interest was put on lanthanide MOFs [3] due to their interesting photophysical properties, permitting possible applications from chemical sensors to medical imaging. In particular, the preparation of MOFs based on europium/terbium and terephthalic acid, in two different DESs ChCl:urea (1:2) (reline) and ChCl:e-urea (1:2), was explored, underlining the impact of the used solvents [4]. Indeed, with reline, only one structure was obtained, while with ChCl:e-urea multiple new structures were obtained as a pseudo-polymorphic MOF system. This difference in behavior, explained by the coordination of the solvent molecules, showed that DESs directly impact the crystallization with an important templating and structuring effect permitting access to new MOF systems directly depending on the nature of the chosen DES.

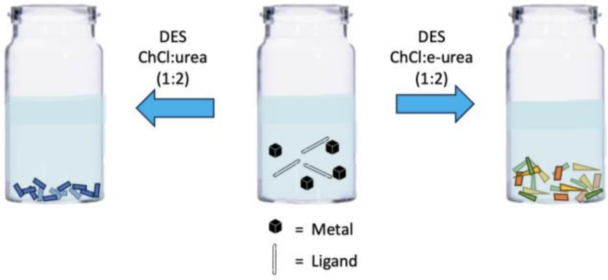

Fig. 1. Impact of the chosen DES

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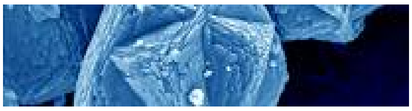

THEME

☒ Theme 1: Synthesis and shaping

☐ Theme 2: Applications for the environment, energy, and health

☐ Theme 3: Characterization and modelling

Upscaled Al-fumarate synthesis and shaping by spray drying

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Aluminium-based MOFs, are promising candidates for various applications such as water harvesting[1] or thermal heat management[2]. However, significant obstacles remain in the synthesis of these materials, including the use of toxic solvents, harmful reagents, demanding pressure and temperature conditions, and their susceptibility to degradation in humid air. These challenges hinder the scalability of their production and limit their industrial applications.

Our study introduces an efficient, upscaled synthesis of Al-fumarate via spray-drying, a process that combines synthesis and work-up into a single step. This all-in-one synthesis method produces high-quality, calibrated Al-fumarate grains without the need for further processing (Figure 1). Unlike previously reported aqueous-phase synthesis routes that require basic conditions (e.g., NaOH addition[3]), the approach presented here operates at a pH below 3. The use of aluminium isopropoxyde as a base enables a steady reaction with fumaric acid without requiring pH adjustment. Structural analysis reveals major differences in the meso- to macroporous structure depending on the drying process: the spray-dried pilot batch exhibits high-density characteristics with an absence of intergranular porosity, unlike other drying techniques. We show here a demonstration at pilot scale using an industrial sized spray-drier allowing production of 10 kg/h.

As a proof-of-concept, air dehumidification was performed in a fluidized bed, highlighting its advantages over fixed beds. The fluidized bed's superior heat transfer ensures greater isothermicity, as demonstrated by the breakthrough curve profile, which shows a longer $t_{50\%}$ and confirms improved column isothermicity.

Ultimately, we developed a comprehensive 3-in-1 process that integrates synthesis, drying, and shaping, while also demonstrating its potential for production intensification. This synthesis approach could pave the way for the scalable production of other aluminium-based MOFs, a topic currently under investigation.

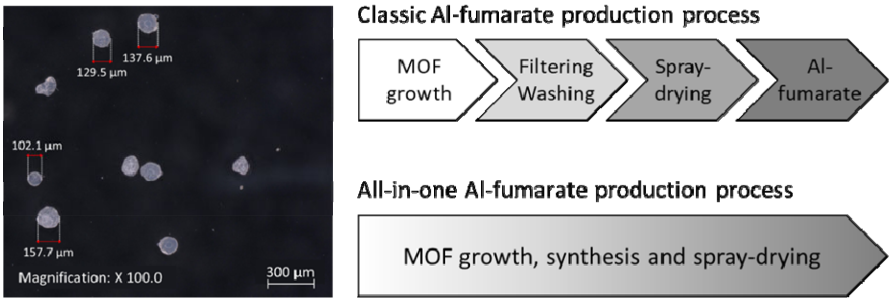

Fig. 1. Calibrated al-fumarate dense spheres obtained at the spray-drier pilot at Axel'One (left) and schematic representation of the all-in-one designed synthesis process (right).

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☒ Theme 1 : Synthesis and shaping

THEME ☐ Theme 2: Applications for the environment, energy, and health

☐ Theme 3 : Characterization and modeling

Role of the Zeolite Counter-Ion in Controlling the Synthesis of Zeolite-Templated Carbons

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Zeolite-Templated Carbons (ZTCs) represent a class of highly porous and nanostructured carbon materials synthesized via a negative replication methodology employing zeolite as templates. These advanced carbon materials exhibit remarkable potential across diverse technological domains, including energy storage, gas storage and separation, and electrocatalytic applications [1].

Previous investigations have allowed to explore critical synthesis parameters such as concentration of zeolite acid sites and synthesis temperature [2,3]. Yet, the influence of zeolite counter-ions on ZTC properties remains largely underexplored.

In this work, we investigate how the choice of zeolite counter-ion influences the properties of ZTCs through a systematic study based on EMT zeolites featuring H^+, Na^+, and Ca^{2+} counter-ions. Although all zeolites can act as templates for ZTCs, the textural and chemical features of the resulting materials differ markedly. Notably, the ZTC derived from Na-EMT exhibits broad diffraction peaks, indicative of diminished textural quality and reduced carbon incorporation within the zeolite template (Figure 1a). These factors suggest the presence of textural defects, as further supported by nitrogen physisorption measurements (Figure 1b). These observations might be related to the very low acidity of the sodium cation, which limits efficient carbon skeleton condensation, as evidenced by Raman spectroscopy.

Although the ZTCs derived from H^+ and Ca^{2+} exchanged EMT both exhibit high textural properties, H-EMT proves to be a slightly less efficient template. This finding is possibly linked to the presence of strong Brønsted acid sites, which lead to enhanced reactivity and, hence, to the development of more textural defects. In contrast, the ZTC derived from Ca-EMT, featuring moderate acidity, shows a strong XRD long-range order, replicating five distinct planes of the original EMT zeolite. Notably, this sample also demonstrates the highest electrical conductivity.

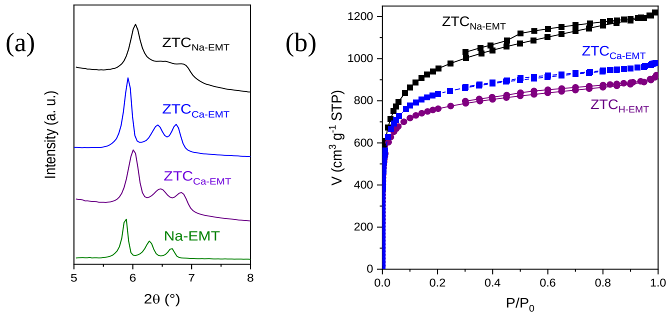

Figure. 1. (a) N_2 Physisorption at 77 K and (b) XRD patterns of ZTCs derived from H^+, Na^+, and Ca^{2+} EMT zeolites, illustrating the influence of the counter-ion on the long-range order of the resulting carbons.

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THEME

☒ Theme 1 : Synthesis and shaping

☐ Theme 2: Applications for the environment, energy, and health

☐ Theme 3 : Characterization and modeling

Design and synthesis of a stable porous Porphyrinic Zirconium MOF for applications in photocatalysis

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In recent years, porphyrin-based and porphyrin-containing metal organic frameworks (noted PMOFs) have particularly attracted attention for their photoactivity. [1,2] Inspired by the enhanced hydrophobicity and higher stability to oxidation and light on fluorinated MOFs, [3,4] we have ignited an effort to explore the synthesis and functional properties of fluorinated PMOFs. Specifically, we developed the gram scale synthesis of the fluorinated analog of the tetrakis(4-carboxyphenyl)porphyrin (TCPP), named F$_{16}$TCPP to be used as linker.

It is established that the strong interaction between Zr(IV) and carboxylate make the resultant MOFs chemically stable, bearing this in mind, we constructed a polyfluorinated porphyrinic zirconium MOF by combining Zr precursor and F$_{16}$TCPP (5,10,15,20-tetrakis-(4-carboxy-2,5,6-tetrafluorophenyl)porphyrin) through adjusting the reaction conditions. By carefully choosing different metal precursors and exploring the reactivity in different solvents, a new Zr-FPMOF could be isolated in a reproducible manner with good yield. Synchrotron diffraction data revealed that Zr-FPMOF crystallizes in the space group *P*432, the structure is arranged in cubes formed of eight corner-sharing $Zr_6O_4(OH)_4$ units and six face-sharing F$_{16}$TCPP porphyrin units, leading to a cubic structure and ~19.3 Å pore size. The topology of this framework can be classified as a 3-D (4,12)-connected **ftw** net. The Schematic Diagram of this novel porphyrinic MOFs synthesis is shown in Fig. 1.

In this flash communication, relevant structural, spectroscopic and textural properties characterizations will be detailed. The materials physical properties and relevant applications are now being explored through collaboration.

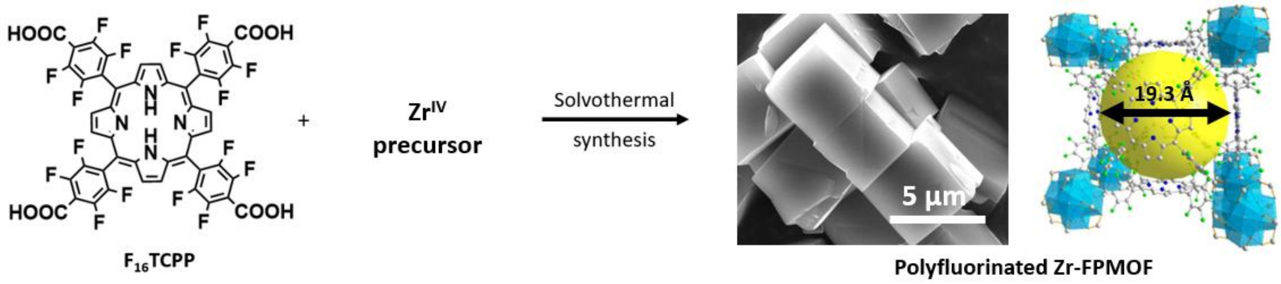

Fig. 1. Schematic Diagram of Polyfluorinated PMOF synthesis.

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THEME

☒ Theme 1 : Synthesis and shaping

☐ Theme 2: Applications for the environment, energy, and health

☐ Theme 3 : Characterization and modeling

Synthesis of nanosized zeolites for detection of VOCs

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The detection of volatile organic compounds (VOCs) is critical in various fields such as environmental monitoring, industrial safety, and healthcare, requiring efficient detection and subsequent elimination [1]. Zeolites have been considered for gas sensing applications due to their unique properties, including different pore sizes and shapes, large surface area, high adsorption capacity, excellent selectivity, and diverse hydrophilic/hydrophobic characteristics [2].

In this study we investigated the adsorption behaviour of zeolites with an MFI framework for characteristic VOCs including acetone, isopropanol, and hexane on using in situ Fourier Transform Infrared (FTIR) spectroscopy. Two different MFI- nanozeolite samples, one as pure silica (Si-MFI) and the other Mo-containing (Mo-MFI) with varying particle sizes (ranging from 100 nm to 2 µm), were synthesized and characterized thoroughly by XRD, SEM, FTIR prior to their evaluation by in situ IR spectroscopy.

A comparative analysis of adsorption kinetics and capacity provided insights into the zeolite's selectivity and efficiency for VOC capture. The results revealed pronounced differences in the adsorption behaviour of hexane, acetone, and isopropanol on Mo-containing and pure silica zeolites. Acetone exhibited strong hydrogen bonding interactions with silanol groups of the zeolite structure, as evidenced by the consumption of isolated hydroxyl groups, whereas isopropanol and hexane demonstrated varying degrees of physisorption dominated by their molecular polarity and size.

This research offers a comprehensive understanding of VOC-zeolite interactions, paving the way for the design of advanced materials for environmental monitoring and industrial safety applications.

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POSTERS
THEME 2

THEME

☐ Theme 1 : Synthesis and shaping
☒ Theme 2: Applications for the environment, energy, and health
☐ Theme 3 : Characterization and modeling

Valorisation of Greenhouse and Acid Gas by Low-Silica Zeolite Catalyst

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The increasing emissions of greenhouse gases such as CO_2 into the atmosphere demand mature technologies to convert CO_2 into value-added compounds. Refineries and petrochemical industries emit 1.24 Pty of CO_2 and process large quantities of hydrogen sulfide (H_2S). The admixture of H_2S with CO_2 is called "acid gas".[1] No existing technologies allow simultaneous reduction of CO_2 and H_2S. A new technology aims to electrify simultaneous conversion of acid gas components into platform molecule carbonyl sulfide COS, which is further converted into CO and marketable Sulphur.[2] The COS formation in continuous mode from CO_2 and H_2S is the first and most important stage of this process ($H_2S(g) + CO_2(g) \rightleftharpoons COS(g) + H_2O(l)$). Zeolites catalyze this reaction via dissociative adsorption, leading to over 70% conversion of H_2S. The benchmark catalyst for this reaction is zeolite NaX[3], yet the literature lacks devoted efforts to optimize this reaction. In this work, we explore different zeolites for COS formation, aiming to develop a catalyst that gives high COS yields per pass and low energy demand for regeneration. A fixed-bed quartz reactor was used for this reaction and four zeolites in two states were used (i) fully dry and (ii) water-saturated.

Table 1. Properties of zeolite catalysts employed in this work.

Material	Si/Al ratio	$S_{BET}(m^2/g)$	Density (g/ml)	Hydration (%)
13X	1.2	900	0.65	24
4A	0.97	400	0.4	20.6
Y	2.5	700	-	23.8
13X-K (potassium-exchanged 13X)	1.2	900	0.65	21.5

The COS formation is minimum on zeolite Y amongst all dry zeolites. Despite having the same framework as that of zeolite Y, 13X has very high conversion followed by slower deactivation. Zeolite 4A outperforms all the catalysts, giving the maximum COS yield during the first hour of the reaction (Fig 1), followed by a deactivation faster than that of 13X and 13X-K. The activity of 13X-K is intermediate between 13X and 4A. The catalytic tests at a range of temperatures i.e., 45-350°C are carried out to study the effect of temperature. As water is one of the reaction products, zeolite deactivates due to the poisoning of the active sites by water[4], which was confirmed in this work by the negligible activity on water-saturated zeolites. Therefore, we systematically evaluate the hydration level of these zeolites and its role in COS formation.

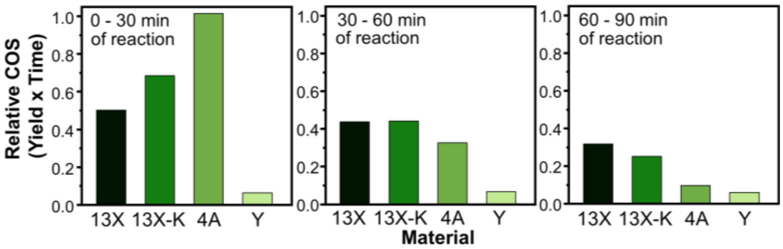

Fig 1. Relative COS formed at 100°C over dry zeolites at different times on stream (TOS).

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THEME

☐ Theme 2: Applications for the environment, energy, and health

A Versatile Cerium MOF with 1-D Open Metal Sites for Catalysis

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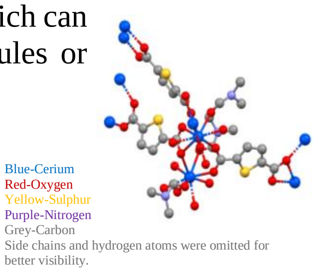
In recent years, metal–organic frameworks (MOFs) have gained attention for their applications in separation, storage, and catalysis.[1] The combination of appropriate metal cations and organic linkers often results in the formation of open metal sites (OMSs), which can play diverse roles, including acting as coordination sites for guest molecules or contributing to catalytic properties.[2]

In this study, we synthesized a cerium(III)-based MOF (Ce-H$_2$TDC) (Fig.1.) using both microwave-assisted and solvothermal methods. Cerium MOFs are particularly advantageous due to their ability to facilitate redox reactions, which enhance their catalytic activity.[3] Moreover, lanthanide-based MOFs are known to yield very stable MOF's, due to their high coordination number.[4] The microwave-assisted synthesis produced the MOF in powder form, while the solvothermal method yielded a microcrystalline material. Both methods exhibited the same XRD patterns, confirming correlation between the two synthesis methods, while the microwave method significantly reduced the reaction time from one day to 20 min. The most characteristic feature of Ce-H$_2$TDC is its 1-D zigzag chains of metal cations with Ce–Ce distances of 4.137 Å, coordinated by DMF from the same direction, enabling densely aligned 1-D OMSs upon DMF removal.



Blue-Cerium
Red-Oxygen
Yellow-Sulphur
Purple-Nitrogen
Grey-Carbon
Side chains and hydrogen atoms were omitted for better visibility.

Fig. 1. The molecular structure of Ce-H$_2$TDC (view from c axis)

The acidity of the material was evaluated using NH$_3$-TPD, which revealed the three distinct desorption peaks at approximately 290°C, 324°C, and 379°C, thus indicating the presence of acidic sites of varying strength. Thermogravimetric analysis (TGA) showed the MOF decomposes at 450°C, confirming its high thermal stability. Interestingly, although the MOF exhibits 10×17 Å, pores characteristic of its 3D structure, its surface area is relatively small (9 m^2/g) and CO$_2$ adsorption capacity is around 1 mmol/g at 273K, 1.2 bar. This disparity may arise from pore collapse due to breathing or other effects, yet the pore dimensions and aligned OMSs remain advantageous for catalytic applications.

The nickel-exchanged cerium-based MOF (Ni-Ce-H$_2$TDC) was synthesized to enhance its catalytic activity for the methanol-to-dimethyl ether (MTD) process at 280°C, with a WHSV of 1.69 h^{-1}. Nickel was introduced to improve the MOF's ability. The material achieved 99% methanol conversion within 30 minutes and maintained complete conversion (100%) up to 8 hours of reaction time (Fig.2.) Small amounts of byproducts, such as CH$_4$ and CO, were observed at 5 and 8 hours but did not affect the overall conversion.

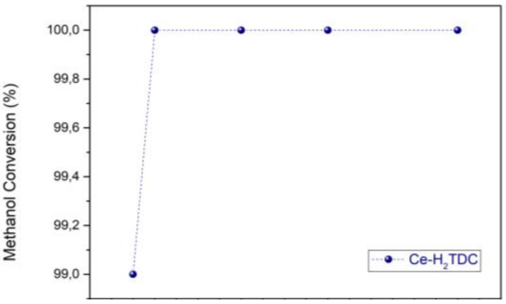


Fig. 2. Methanol Conversion vs Time for Ni-Exchanged Cerium MOF at 280°C

In conclusion, the cerium-based MOF showed good stability and catalytic performance, with the nickel-exchanged version improving its activity and long-term stability, supported by its structure.

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THEME

☐ Theme 1 : Synthesis and shaping

✓ Theme 2: Applications for the environment, energy, and health

☐ Theme 3 : Characterization and modeling

Nano zeolite-based polyamide composite membrane for desalination

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Abstract

Freshwater scarcity has become one of the most pressing issues worldwide. Nanofiltration, as an efficient, energy-saving, and easily integrable membrane separation technology, has been widely applied in fields such as water treatment and clean energy production. However, the "trade-off" effect between permeability and selectivity remains a significant bottleneck for advancing membrane technology. Traditional thin-film composite (TFC) polyamide membrane are typically synthesized via interfacial polymerization reactions between polyamines and acyl chlorides. In this study, we introduce nano-zeolite interlayer (SOD zeolite/GO composite interlayer or EMT zeolite interlayer) to regulate the storage and release behavior of amine monomers. This approach slowed down the interfacial polymerization process, enabling the formation of interlayer-based thin-film composite membrane (i-TFC) with an ultra-thin and dense polyamide layer. The resulting membrane exhibited significantly enhanced pure water permeability (increased by 200%) and membrane structure stability. Additionally, the inorganic porous interlayers endowed the nanofiltration membranes with good structural stability (pressure resistance and anti-fouling properties). This work provides a novel strategy for regulating high-performance nanofiltration membranes, enhancing the separation process.

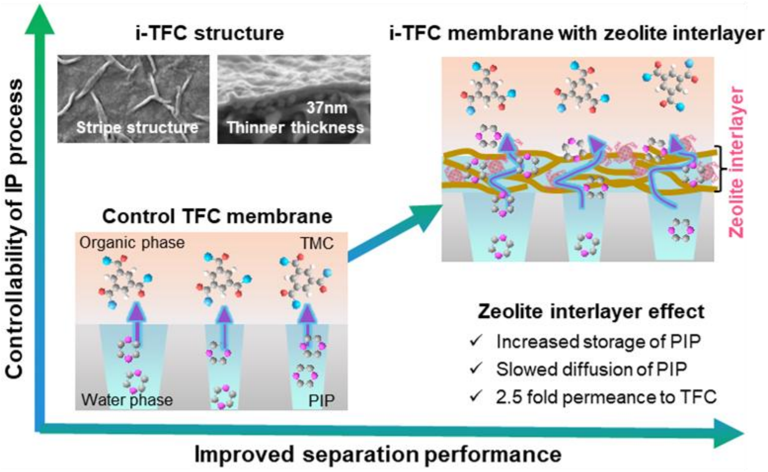

Fig. 1. Schematic diagram of the monomer interfacial polymerization process regulated by the functional nano-molecular sieve intermediate layer

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☐ Theme 1 : Synthesis and shaping

THEME √ Theme 2: Applications for the environment, energy, and health

☐ Theme 3 : Characterization and modeling

Tuning Co^0/CoO ratios of Co/MFI catalysts for CO_2 hydrogenation to ethanol via zeolite framework tetrahedral aluminum

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The hydrogenation of CO_2 to ethanol offers a promising pathway for mitigating CO_2 emissions. In Co-based catalysts, the coexistence of Co^0 and CoO is essential for efficient catalytic activity [1]. The optimization of the Co^0/CoO ratio is a key factor in enhancing catalytic performance. In this study, the Co^0/CoO ratio was modulated through the tetrahedral Al within the framework of MFI zeolite supports. The tetrahedral Al reduces the cobalt adsorption energy on the zeolite, thereby enhancing metal-support interactions and providing reduced Co/MFI catalysts with lower Co^0/CoO ratios. This approach enables the Co^0/CoO ratio to be precisely controlled by adjusting the Si/Al ratio of the zeolite. As the Si/Al ratio decreases from ∞ to 40, the Co^0/CoO ratio in the reduced catalysts decreases from 1.86 to 0.8. Catalytic performance tests revealed the ethanol selectivity and space-time yield of ethanol (STY) exhibited an approximate volcano-type relationship with the Co^0/CoO ratios. The Co/MFI catalyst with a Co^0/CoO ratio of 0.96 exhibited the highest ethanol selectivity (17%) and space-time yield (STY) of 0.92 $mmol_{EtOH}\cdot g_{cat}^{-1}\cdot h^{-1}$ at 250°C and 2 MPa. This study provides a viable strategy for fine-tuning Co^0/CoO ratios by tetrahedral aluminium and delivers valuable guidance for the design of catalysts for CO_2 hydrogenation to ethanol.

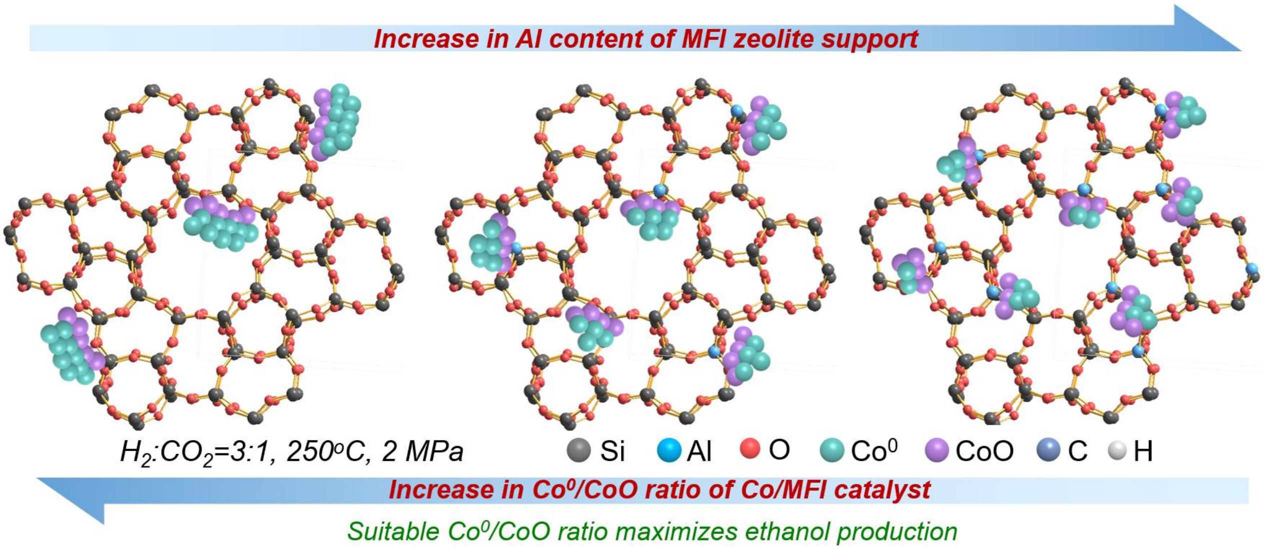

Fig. 1. The Co^0/CoO ratios can be tuned simply by Si/Al ratios of MFI zeolites.

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THEME

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Investigating the impact of monovalent alkali metal incorporation on the properties of ZSM-5 zeolites

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The increasing demand for light olefins (C_2–C_4) in the petrochemical industry has been alleviated by the successful implementation of the methanol-to-olefins (MTO) process[1]. H-ZSM-5 zeolites are efficient MTO catalysts[2-4]. However, their strong acidity promotes undesirable hydrogen transfer reactions, leading to accelerated coke formation and thus rapid deactivation[5].

To face this issue, alkali metal-doped M-ZSM-5 zeolites (M: Li, Na, K) were synthesized via impregnation and characterized by ICP, XRD, SEM, N_2 adsorption-desorption, XPS and NH_3-TPD to evaluate their elemental composition, structure, morphology, specific surface area, pore volume and acidic properties. Their catalytic performances were evaluated in the MTO reaction with the aim to decipher the role of the metal cations on the catalyst stability and light olefins selectivity. The results showed that alkali metal doping did neither alter the zeolite structural and textural properties, as expected decreased the acid site density. Besides, DFT calculations were undertaken to rationalize the interaction between the cation and light olefins. It is suggested that an olefin-cycle mechanism, preventing hydrogen transfer reactions, is favored over the latter alkali-exchanged catalysts. Hence, higher propylene and butylene selectivities and prolonged catalyst lifetimes could be achieved over M-ZSM-5 series. Amongst them, Li-ZSM-5 exhibited the best performance, yielding C_2–C_4 light olefins selectivity of 71%, being 10% higher than pristine H-ZSM-5, as well as an extended lifetime of 5 h.

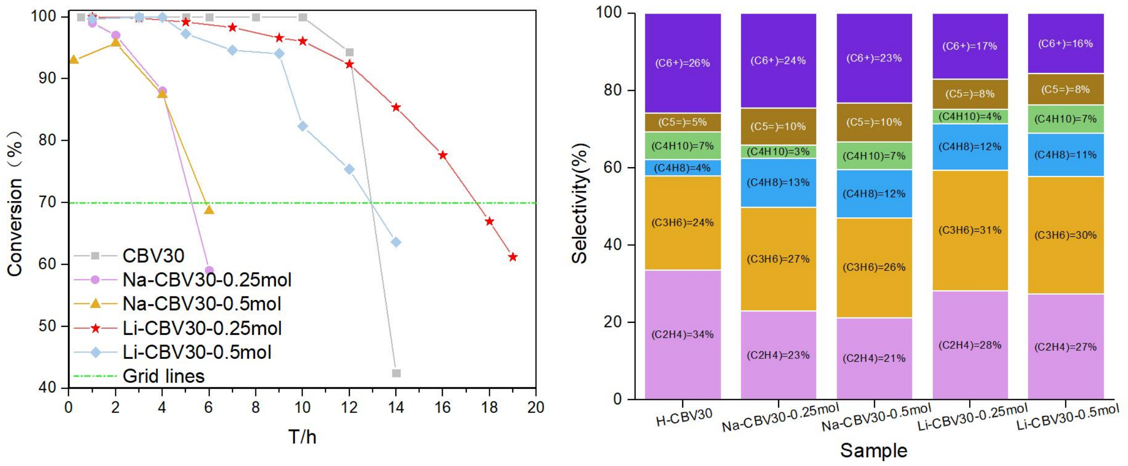

Fig. 1 Methanol conversion and Selectivity in the different hydrocarbons over alkali-modified ZSM5 zeolites

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THEME

☐ Theme 1 : Synthesis and shaping
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Enhancing chlorine removal from pyrolysis oils using FAU zeolites

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Chemical recycling of plastics into pyrolysis oils enables the production of recycled polymers. Residual impurities in these oils can be removed through ex-situ adsorption using zeolites, which effectively eliminate organochlorine compounds [1]. This occurs via an interaction between the basic oxygen in the zeolite framework and the hydrogen from the chlorine-bound carbon [2]. This communication explores the impact of the Si/Al ratio and the composition of FAU-type zeolites on the removal of chlorine from pyrolysis oils, in both batch and fixed-bed processes. The selectivity of zeolites for chlorine decreases when applied to industrial pyrolysis oils, due to numerous competitors occupying the adsorption sites adjacent to the organochlorine compounds. It is essential to consider the oil composition when adjusting the chemical properties of the adsorbent to minimize competitive effects and maintain selectivity for organochlorines. Our findings indicate that the selectivity of zeolites for organochlorines significantly declines when new competitors are introduced into the model oil (Fig. 1). The higher Si/Al ratio in Na-Y zeolite negatively affects dechlorination due to the reduced number of cations present (Fig. 1). With no cations in sites III, aromatic adsorption is strongly favoured in Na-Y zeolite, which prevents organochlorine adsorption in the same supercage because of steric hindrances. Notably, our findings show that K-exchanged zeolite exhibits the highest chlorine adsorption when alkenes and aromatics are present (Fig. 1). This can be attributed to the size and position of K^+ cations, which are less favourable for the adsorption of aromatic and olefinic compounds. Modulating the acid-base properties and the position of cations in FAU zeolites through various cation exchanges enhances selectivity for organochlorine compounds.

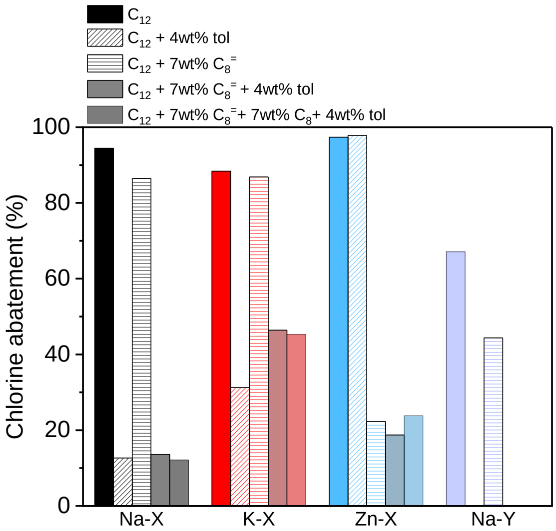

Fig. 1. Effects of competitions on the chlorine abatement of FAU-exchanged zeolites

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THEME

☐ Theme 1 : Synthesis and shaping
☒ Theme 2: Applications for the environment, energy, and health
☐ Theme 3 : Characterization and modeling

BTX and ZIF-8: A Case of Strong Adsorption

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The quest for technological innovations to capture Volatile Organic Compounds (VOCs), particularly aromatic compounds such as benzene, toluene, and xylene (BTX), remains ongoing.[1] While Activated Carbon (AC) is the state of the art adsorbents, it suffers from rapid desorption upon heating. Actually, an increase of few degrees causes the release of accumulated VOCs, resulting in peak pollution concentrations. We investigated the adsorption-desorption performance of two Metal-Organic Frameworks (MOFs), ZIF-7 and ZIF-8, which exhibit structural and local-type flexibility, respectively, triggered by guest-host interactions.[2-3]

We assessed their capacity for BTX adsorption using both static and dynamic methods. Unlike traditional AC, ZIFs maintain their adsorption performance in the presence of water. Nevertheless, notable differences concerning desorption between these two ZIFs must be noted. ZIF-7, similar to AC, shows significant desorption at low temperatures (Fig. 1a-b). This characteristic potentially leads to high VOC release when exposed to solar radiation, making it unsuitable for indoor air treatment. On the other hand, and as far as ZIF-8 is concerned, no significant BTX desorption at temperatures below 50°C occurs, while excellent regeneration characteristics at higher temperatures are maintained (Fig. 1c). We suggest that ZIF-8's specific property can be explained by a local dynamic motion mechanism. Toluene is strongly diffusion-controlled, requiring the molecule to overcome a high energy barrier to cross the narrow 6-membered ring (6-MR) aperture. Interestingly, the size of this aperture is reduced by the linker, induced by toluene packing in the SOD cavity.

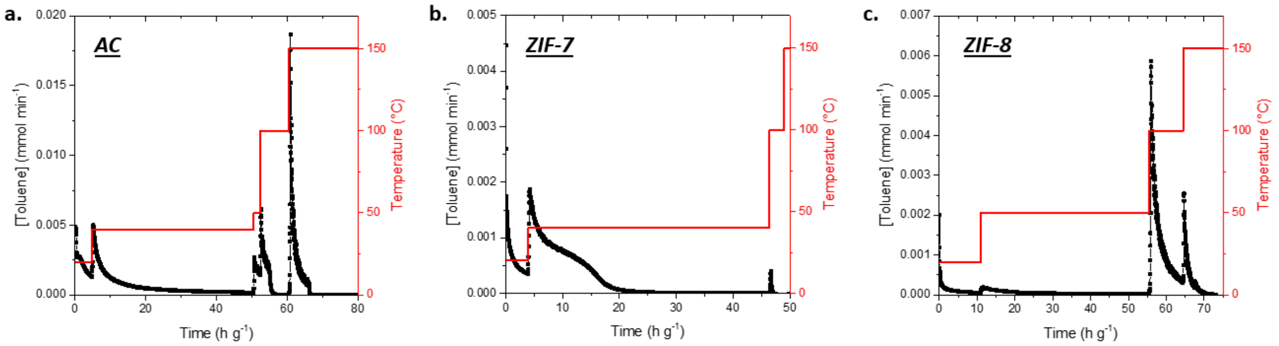

Fig. 1. Profile desorption of toluene on AC (a), ZIF-7 (b), and ZIF-8 (c) at different temperatures.

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THEME

☐ Theme 1: Synthesis and shaping

☒ Theme 2: Applications for the environment, energy, and health

☐ Theme 3: Characterization and modeling

Plastic pyrolysis using extra-large pore zeolite-based catalysts

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The total production of plastic is projected to reach 600 million metric tons by 2025.[1] Knowing that the production of plastics relies on non-renewable resources such as crude oil and its derivatives, and considering that these materials are largely non-biodegradable, the fast increase in plastic production underscores an urgent need for effective plastic upgrading methods. Among the different recycling techniques, catalytic pyrolysis is considered as one of the most promising methods.[2] Notably, zeolite catalysts have attracted special attention due to their well-known porosity and their Brønsted acidity.[3] In the past decade, intermediate (10 MR) and large pore (12 MR) zeolites have been largely investigated as heterogeneous catalysts for plastic pyrolysis indicating a particular catalytic applications in terms of selective diffusion of the reactants or products and of the selective active-site distribution.[4] Although their pores are smaller than those of typical plastic molecules, they exhibit high conversion rates and different selectivity at lower temperatures compared to other catalysts or thermal pyrolysis. Nevertheless, zeolites with larger pores are more than welcome for plastics processing. Over the last few years, new zeolite structures with pore sizes greater than 12 MR channels have been successfully synthesized and stabilized under their acidic forms such as **ZEO-1** (JZO-type)[5] with 16 MR channels (1.4 nm) and **ZMQ-1**[6] with 28 MR channel pores stepping in the mesoporous range (2.3 nm).

The main goal of this work is to investigate the catalytic behaviour of the extra-large pore zeolites toward plastic pyrolysis and upgrading. Low density Polyethylene (LDPE) has been selected as a model for plastic waste. The results obtained are compared with those of commercial intermediate pore: **ZSM-5** (MFI-type) and large pore zeolites Beta, Faujasite (USY samples), and Mordenite (MOR). The investigated zeolites exhibit a wide range of microporous volumes between 0.10 cm^3/g and 0.31 cm^3/g and mesoporous volumes between 0.10 cm^3/g and 0.36 cm^3/g, and a BET surface area in the range of 500-1000 m^2/g.

Catalytic pyrolysis experiments were carried out under a 20 ml/min nitrogen flow rate in a fixed bed reactor with a PE/catalyst= 1. The gaseous and liquid products were analysed online by GC-MS. Additionally, coke deposits are quantified using thermogravimetry (TGA). The conversion rates observed using zeolite catalysts ranged from 80% to 90%, while those obtained for thermal pyrolysis were about 40%. Product selectivity, which varies substantially among zeolites, will be discussed in details.

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THEME

☒ Theme 1: Synthesis and shaping
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☐ Theme 3: Characterization and modeling

Title: Efficiency of porous adsorbents for the selective trapping of I_2/CH_3I in the presence of a large excess of contaminants

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Abstract: The nuclear fuel reprocessing industry releases radioactive isotopes into the environment notably xenon, krypton and iodine. Among these radionuclides, iodine is highly toxic, mobile and volatile in the environment. For radioprotection reasons, it is crucial to develop an innovative iodine trap. As part of the SPECIOSA project, IRSN aims to develop a specific atmospheric sampling device for iodine release monitoring into the environment, ensuring the speciation of physico-chemical forms (I_2 and CH_3I). On the one hand, several commercial porous adsorbents (mesoporous silica, zeolite and activated carbon) were tested for the I_2 adsorption in liquid phase. More particularly, silica and zeolites doping with triethylenediamine (TEDA) and copper was achieved to enhance the affinity towards I_2 at the expense of CH_3I. The obtained adsorption isotherms for I_2 in the liquid phase for these doped materials follow the Langmuir model (Fig.1 A), indicating therefore monolayer and homogenous I_2 adsorption. Promising performances were also noticed especially for the TEDA-doped silica material in terms of both adsorption capacities and trapping affinity. On the other hand, innovative and industrializable MOF formulations are synthesized at UCCS Lille. The obtained powders are shaped by extrusion and spheronization protocols before further tests in gaseous phase (Fig.1 B and C). The extrudates powders were successfully tested with I_2 in the gas phase, showing encouraging performances. The relevant candidates will be tested for CH_3I capture as well as for I_2 under more challenging conditions in agreement with the desired context.

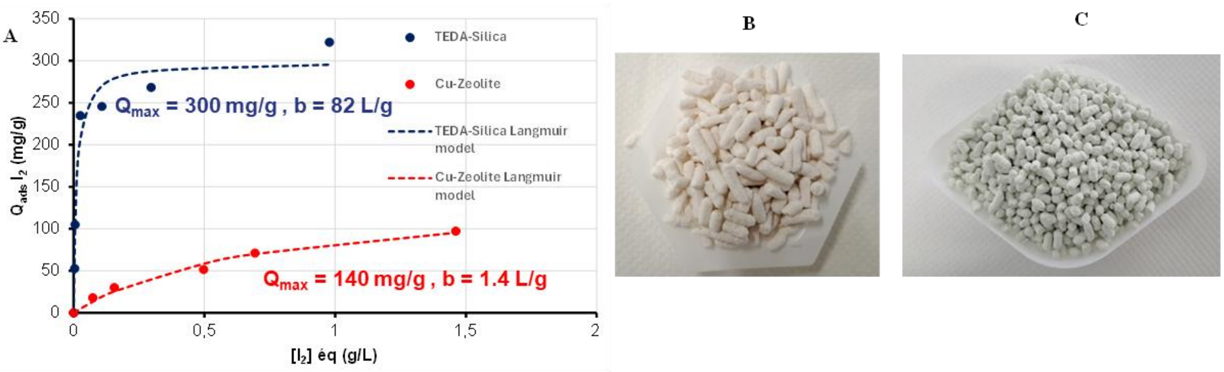

Fig. 1. (A) Liquid-phase adsorption isotherm for I_2 in the presence of TEDA-silica and Cu-zeolite (B) MOF 1, (C) MOF 2

THEME

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☐ Theme 3 : Characterization and modeling

The Encapsulation of Curcumin in Aluminum Fumarate Metal-Organic Frameworks for Improved Stability and Antioxidant Activity

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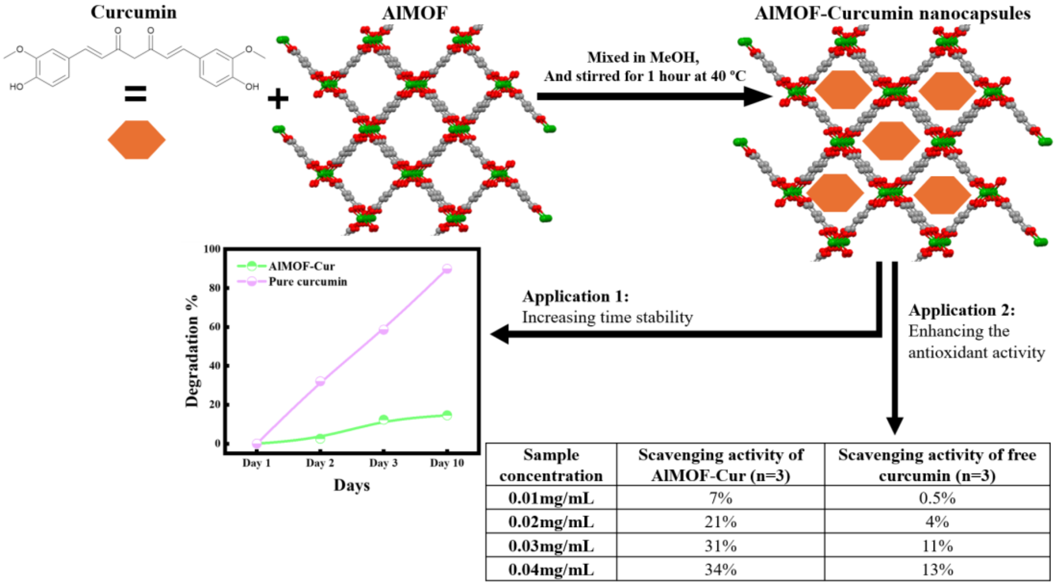
Curcumin (Cur) is a promising candidate for antioxidant applications;[1] however, due to its limited solubility and low bioavailability,[2] it remains only hardly employed as a therapeutic agent. Moreover, curcumin is very unstable and exhibits a rapid degradation. Metal–organic frameworks (MOFs) have gained great interest in the field of drug loading due to their diversity and tunability,[3] so they are seen as great structures for hosting curcumin. In this study, aluminum fumarate MOF (AlMOF) was able to encapsulate curcumin successfully by the wet impregnation method. The resulting system significantly improved the stability of curcumin, so it went from degrading to 58.9% after 3 days to degrading to 16% after 10 days when entrapped in AlMOF. In addition, the antioxidant activity of curcumin was enhanced in the obtained system compared to free curcumin. These results open the door to an in-depth study of MOF-Cur systems as great therapeutic agents due to the enhancement of the antioxidant properties of curcumin, all while favoring its solubility, and maintaining its stability.



Sample concentration	Scavenging activity of AlMOF-Cur (n=3)	Scavenging activity of free curcumin (n=3)
0.01mg/mL	7%	0.5%
0.02mg/mL	21%	4%
0.03mg/mL	31%	11%
0.04mg/mL	34%	13%

Fig. 1. Schematic representation of curcumin loading into AlMOF by the wet-impregnation technique, resulting in a reduced degradation % and a boosted scavenging activity.

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THEME

☐ Theme 1 : Synthesis and shaping
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☐ Theme 3 : Characterization and modeling

"ZIF-25–water": a novel high-performance shock-absorber system revealed through high-pressure intrusion experiments

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The potential of lyophobic heterogeneous systems for storing, dissipating or absorbing mechanical energy was initially explored by Eroshenko [1]. The energetic performances of these systems, consisting of a lyophobic solid porous material immersed in a non-wetting liquid, are determined through high-pressure intrusion-extrusion experiments. With water as the non-wetting liquid, we previously highlighted the spring-like and shock-absorber behaviors of two Zeolitic Imidazolate Framework (ZIF) materials, ZIF-8 (**SOD** topology) and ZIF-71 (**RHO** topology), respectively [2, 3].

In order to assess the impact of the material's chemical composition on the energetic performances of the "ZIF–water" systems, ZIF-25 was selected for study. This metal-organic framework displays the **RHO** topology with the formula $Zn(dmim)_2$, where dmim stands for 4,5-dimethylimidazolate). Optimising the synthesis of ZIF-25 was a prerequisite and achieved *via* a solvothermal route using acetic acid as a modulating agent.

The micrometric particles obtained made possible, for the first time, the complete structural resolution of ZIF-25, from powder X-ray diffraction using the Rietveld method. ZIF-25 crystallizes in the space group $Pm\bar{3}m$ with a lattice parameter a = 28.5668(2) Å. Its micropore volume is measured at 0.54 cm^3/g and its BET surface reaches 991 m^2/g. Moreover, high-pressure water intrusion-extrusion tests reveal that the "ZIF-25–water" system acts as a molecular shock-absorber capable of absorbing 16 to 19 J/g of energy and restoring 10 J/g. It is worth noting that similar behaviour has previously been observed for ZIF-71, which shares the same **RHO** topology [4]. In conclusion, this study helps importantly to show that the energetic behaviour of ZIFs-based lyophobic systems is topology-dependent.

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THEME

☐ Theme 1 : Synthesis and shaping

☐ Theme 2: Applications for the environment, energy, and health

☐ Theme 3 : Characterization and modeling

Optimized Nanosized Zeolite P for Faster CO_2 Adsorption Kinetics

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Slow adsorption rates in zeolites present a challenge for industrial applications, which can be addressed by downsizing zeolite crystals to enhance surface area and reduce diffusion pathways [1, 2]. This study reports a template-free seed-assisted synthesis of nanocrystalline zeolite P1 with a GIS-type framework, achieved using minimal seeds, lower temperatures, and shorter reaction times, resulting in pure NaP1 as spherical nanoaggregates (**Fig.1**).

Potassium-exchanged nanosized KP1 exhibited superior CO_2 adsorption capacity (1.9 mmol/g) and faster kinetics compared to micron-sized KP2, which showed slower diffusion limited by surface barriers. The trapdoor effect, facilitated by K^+ cation displacement, enabled exceptional CO_2 selectivity over N_2 and CH_4. Static and dynamic adsorption studies revealed KP1's significantly 93 times faster adsorption rate than the micron-sized counterpart and enhanced diffusion due to its smaller particle size and intra-crystalline diffusion mechanisms. These findings underscore the potential of nanosized K-exchanged zeolites for efficient CO_2 capture and separation in industrial applications [3].

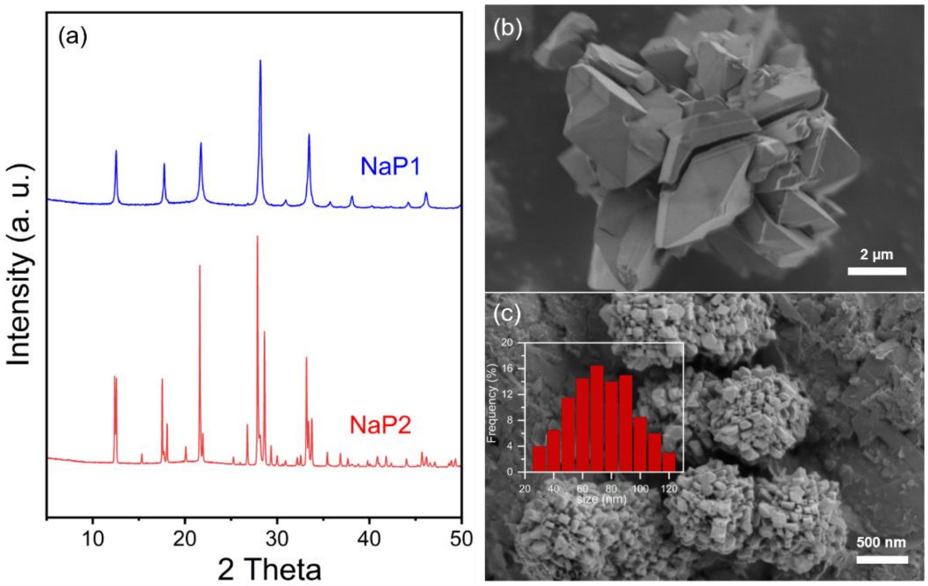

Fig. 1. XRD patterns of as-synthesized zeolites (a) and SEM images of micron-sized NaP2 (b) and nanosized NaP1 (c).

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THEME

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Fe-MFI-supported Ni for CO_2 hydrogenation in the power-to-gas process

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The Power-To-Gas process is a relatively novel and efficient way of storing excess energy from non-programmable renewable energy sources, such as wind and photovoltaic, in chemical form. This process allows for significant metal economy, when compared to batteries. It involves the emission of H_2 from water electrolysis, and its direct conversion into methane by CO_2 hydrogenation. The light hydrocarbons obtained from the process are valuable building blocks for further chemical processes.

The present work aims to produce catalysts adapted for the CO_2 hydrogenation step. While ceria-supported nickel catalysts showed promise[1], metal-containing zeolites offer major advantages, such as metal economy and high adsorptive and catalytic properties. Furthermore, the bimetallic combination of Fe and Ni species offers the possibility for a shift in selectivity towards C_2^+ products, which are even more desirable than methane[2].

Fe-MFI nano-sized zeolites (150 – 300 nm) were synthesized (**Figure 1a**) adapting a protocol proposed by Zhang *et al.*[3] to an autonomous synthesis robot composed of interconnected modules (pipetting, powder handling, mixing, shaking, heating up to 190°C, pH station, centrifugation, filtration…). Fe framework integration was confirmed by XRD, FTIR and NEXAFS analysis, the latter technique indicating the sole presence of Fe (III) species (**Figure 1b**). Further work will explore the full impact of synthesis conditions using the synthesis robot on the catalyst (Fe content and salt, water volume, OSDA, stirring speed, etc.). Nickel impregnation and ion exchange will be performed, and the final catalysts will be evaluated for CO_2 hydrogenation reaction. Literature suggests a distinct activity of Ni (II) species in addition to the usual Ni (0) species, and should be evidenced through this work. Finally, the Fe-Ni(0 vs II) interactions and their impact on C_2^+ products selectivity will be surveyed.

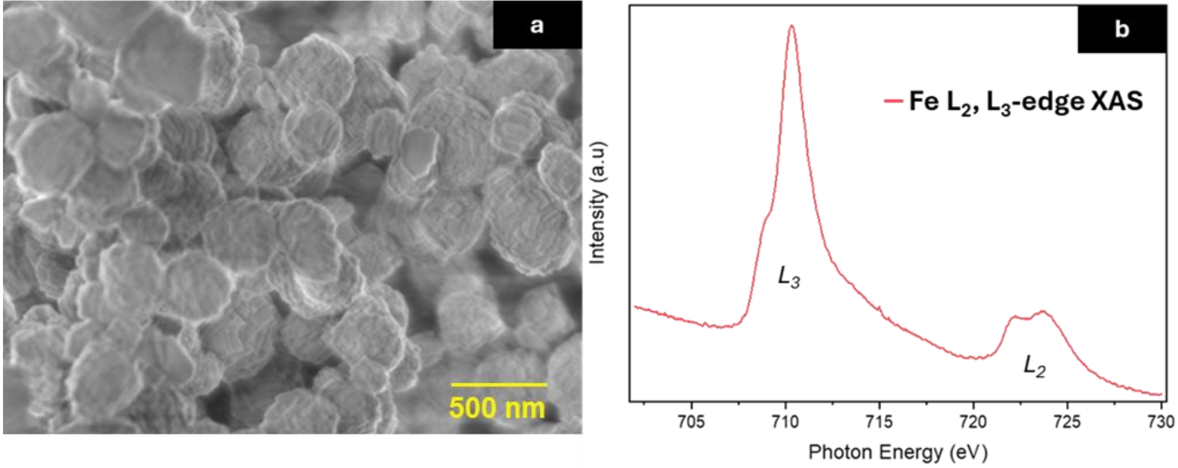

***Figure 1**: **a** - SEM imaging and **b** - Fe $L_{2,3}$-edge spectra of the as-synthesized nano-sized Fe-MFI*

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THEME

☐ Theme 1 : Synthesis and shaping

☒ Theme 2: Applications for the environment, energy, and health

☐ Theme 3 : Characterization and modeling

High pressure intrusion of aqueous salt solutions in zeosils: cation influence

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High pressure intrusion of water and aqueous solutions in hydrophobic pure silica zeolites (zeosils) is of high interest for mechanical energy absorption and storage applications. Depending on the zeolite structure, framework stability and the presence of defects, the “zeosil-water” system, when the pressure is released (extrusion), is able to restore, dissipate or absorb the supplied mechanical energy during the compression step (intrusion) and therefore to display a spring, shock-absorber or bumper behavior [1]. The use of aqueous salt solutions can considerably improve the energetic performance of such systems by an increase of the intrusion pressure [2] and even to change the behavior of the system in the case of highly concentrated solutions [3]. However, the mechanism of intrusion of aqueous salt solutions in zeosil micropores is not clearly established. In order to better understand it, the influence of different parameters such as zeosil structure, salt concentration and ion nature on intrusion-extrusion should be studied.

In this work we present a study on the influence of cation nature on high pressure intrusion-extrusion of salt solutions in three different zeosils: chabazite (CHA, 8 MR pore openings), silicalite-1 (MFI, 10 MR) and β (*BEA, 12 MR). The intrusion of aqueous solutions of chloride salts of alkali and alkaline-earth metals (MCl_n, where M^{n+} = Li^+, Na^+, K^+, Rb^+, Cs^+, Ca^{2+}, Mg^{2+}) has been performed. A strong rise of intrusion pressure in comparison with water has been observed for all the zeosils. The pressure increases with cation charge and decreases with its size for alkali metals. These trends are in agreement with cation hydration enthalpy values. Relative increase of intrusion pressure is considerably more pronounced for small pore openings (CHA > MFI > *BEA). Nevertheless, the absolute values of intrusion pressure are higher for silicalite-1 due to its channel structure.

No significant influence of cation nature on behavior of “zeosil – solution” systems has been observed for MFI- and CHA-type zeosils demonstrating a fully reversible intrusion (spring behaviour). However, the behavior changes with cation nature for “*BEA-type zeosil – MCl_n solution” systems. An irreversible intrusion (bumper) is observed for alkali metal chloride solutions, whereas the intrusion of $MgCl_2$ and $CaCl_2$ solutions is partially reversible (combination of bumper and shock-absorber).

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THEME

☐ Theme 1 : Synthesis and shaping

☒ Theme 2: Applications for the environment, energy, and health

☐ Theme 3 : Characterization and modeling

Non-toxic Nanosized zeolites for oxygen delivery and magnetic resonance imaging

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Glioblastoma is characterized by its high resistance to conventional treatments, such as radiation therapy and chemotherapy[1]. This is primarily due to the hypoxic environment, which is a major characteristic of glioblastoma[2]. Therefore, the growing interest in finding efficient oxygen carriers is essential as oxygen is the critical substrate to produce more cytotoxic reactive oxygen species to exert cancer-killing effects2. Nanosized zeolites have emerged as promising platforms for a wide range of medical applications. However, their clinical translation has been hindered by previous synthesis strategies that heavily relied on water as a solvent, limiting their practicality. In this study, we present an innovative synthesis approach for the production of faujasite (FAU) nanosized zeolite crystals, aiming to overcome these limitations and promote the synthesis of safe and sustainable zeolite nanoparticles. Our method exclusively utilizes inorganic structure-directing agents (Na^+) along with a phosphate buffer solution (PBS) as a clinical-grade solvent. By employing PBS instead of water, we successfully enhance the Si/Al ratio within the nanoscale dimensions while preserving crucial characteristics such as crystallinity, microporous volume, and colloidal stability in the PBS buffer. Furthermore, we demonstrate the incorporation of gadolinium into the nanozeolites, enabling the development of contrast agents for magnetic resonance imaging (MRI). In vivo magnetic resonance imaging (MRI) studies confirmed targeted oxygen delivery and gas release within brain tumors, showing a 14.91% difference in cerebral blood volume (CBV) between contralateral brain tissue and tumors after 15 minutes, unlike the control. T1 maps at 7 Tesla showed a relaxation rate of 9.254 $mM^{-1}.s^{-1}$ for PBS-Gd-FAU, twice that of commercial Gd-chelates. The zeolite nanocrystals showed enhanced safety profiles in vitro and in vivo and demonstrated high oxygen capacity with a release rate of 2.68 $mg{\cdot}L^{-1}$ in hypoxic conditions. This zeolite nanocrystals holds the potential to serve as a platform for enhancing tumor oxygenation in anticancer therapy.

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THEME

☐ Theme 1 : Synthesis and shaping

☒ Theme 2: Applications for the environment, energy, and health

☐ Theme 3 : Characterization and modeling

Application of hierarchical zeolites to pesticide remediation in water

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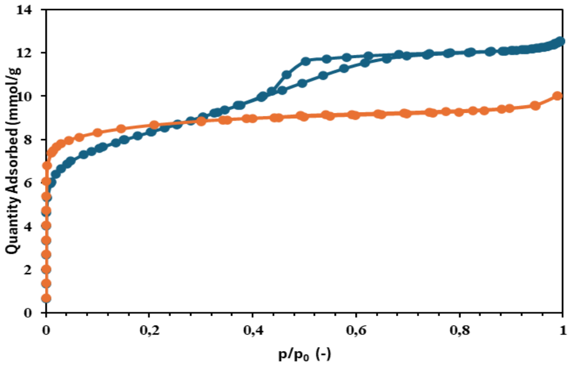
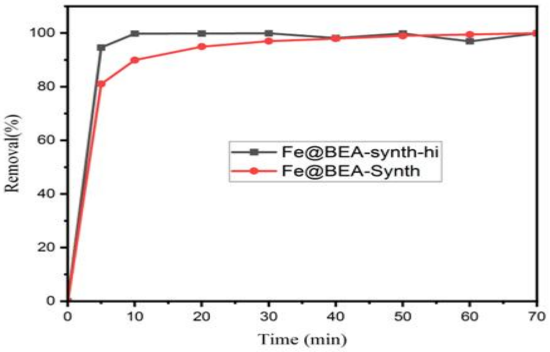
Contamination of aqueous environments by recalcitrant organic pollutants is a major environmental problem worldwide. These compounds, which include dyes, pharmaceutical substances, and pesticides, often originate from industrial, agricultural and urban activities. Chloridazon, also known as pyrazon and classified as an organochlorine herbicide, has been used for sugar beet cultivation until its prohibition in France in 2020 due to the toxicity of its metabolites and their remanence in surface and groundwater bodies as well as in the soil. Several techniques may be used to remediate these metabolites including adsorption, electrochemical, or advanced oxidation processes such as the Fenton process.[1] This process is based on the production of •OH radicals by disproportionation of H_2O_2 catalysed by the redox cycle of Fe^{2+}/Fe^{3+}. Iron salts may be used; however, for water treatment reusable heterogeneous catalysts are preferred to avoid further pollution. Fe_2O_3 supported on zeolites have been applied as photo-Fenton catalysts with interesting performances.[2] However, the intrinsic microporosity of zeolites prevents bulky molecules such as chloridazon' metabolites to diffuse within the zeolite crystals. Thus, only •OH radicals formed on the surface of zeolites can be used to oxidize the metabolites, limiting the degradation efficiency.

This research aims to probe the effect of a hierarchical porous network over the adsorption and degradation kinetics of chloridazon and its metabolites. Two zeolite topologies, MFI and BEA, have been selected. Zeolites with Si/Al ratios of 25 have been prepared, then post-treated to induce the creation of a mesopores as observed by N_2 sorption (Fig 1.a).[3] Then, iron oxide nanoparticles have been deposited on the zeolites before and after hierarchization following the melt infiltration method.[4] As observed in Fig 1.b, above 94.59% of chloridazon and its metabolites were removed after 5 min when using the hierarchical zeolite, against 81% when using purely microporous support thus highlighting the advantage of hierarchical zeolites for this application.





b

Fig. 1. (a) Nitrogen physisorption isotherms of (orange) BEA zeolite and (blue) hierarchical BEA zeolite, and (b) kinetic curves of chloridazon (20 mg/L) degradation.

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THEME

☐ Theme 1 : Synthesis and shaping

☒ Theme 2: Applications for the environment, energy, and health

☐ Theme 3 : Characterization and modeling

Innovative Sorbent Regeneration in Air-Water Harvesting Using MWCNT-Driven Electrothermal Heating

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Freshwater is an indispensable resource providing critical services to nature and society. However, the growing disparity between human demand and freshwater availability has increased water scarcity. Atmospheric water is an alternative resource, thus, adsorption-based atmospheric water harvesting (ABAWH) has emerged as a promising technique to alleviate the current water shortage.

ABAWH systems primarily rely on sorbents' adsorption and desorption of water vapor, making the regeneration process crucial for the ABAWH final performance. Traditional temperature swing regeneration (TSR) and pressure swing regeneration (PSR) techniques require sorbents to possess high thermal conductivity. Unfortunately, most AWH sorbents, like silica gel, hydrogel, aerogel, MOFs, and zeolites, have inherently low thermal conductivity. Compared to conventional TSR and PSR methods, resistive heating regeneration is faster, therefore, allows for rapid adsorbent regeneration. Simultaneously, it can have higher desorption efficiency and requires less energy to achieve a desired desorption level. Nevertheless, the feasibility and performance of resistive heating are highly dependent on the electrical resistivity of the adsorbent. Most vapor adsorbents, including zeolitic materials (resistivity over 10^7 Ω m), have very low electric conductivity.

To address this issue, in this work, we firstly present a promising approach to enhance the thermophysical properties of zeolite extrudates by adding multi-walled carbon nanotubes (MWCNTs). With an optimized composite, the electrical resistivity of the final extrudate is reduced by 9 orders of magnitude to ~0.07 Ω m, enabling rapid electrothermal regeneration useful in AWH systems. Resistive heating tests reveal that MWCNTs-containing extrudate could be heated to 130°C within 2 minutes, with a cooling time of just 1.3 minutes to return back to ambient temperature. These results demonstrate the high feasibility of achieving an ultra-fast and energy-efficient adsorption-desorption cycle in AWH systems. Importantly, no pore blockage or filling is observed during preparation, allowing the final extrudate to maintain optimal properties in the application. This strategy has been successfully implemented across three types of zeolites.

Given the simplicity of the preparation process and the efficacy of the final product, these findings are expected to drive new round innovation in current AWH technology, advancing toward a more efficient and energy-saving generation of AWH systems.

The official presentation will offer comprehensive details.

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THEME

☐ Theme 1 : Synthesis and shaping

☒ Theme 2: Applications for the environment, energy, and health

☐ Theme 3 : Characterization and modeling

Role of hydroxyl groups in Zn-containing nanosized MFI zeolite for the photocatalytic oxidation of methane

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The effective conversion of methane to a mixture of more valuable hydrocarbons and hydrogen under mild conditions is a significant scientific and practical challenge. Here, we synthesized Zn-containing nanosized MFI zeolite for direct oxidation of methane in the presence of H_2O and air. The presence of the surface hydroxyl groups on nanosized MFI-type zeolite and their significant reduction in the Zn-containing nanosized MFI zeolite were confirmed with Infrared Fourier Transform (FTIR) spectroscopy. Incorporation of zinc atoms into the framework of nanosized MFI zeolite is revealed by Nuclear Magnetic Resonance, X-ray Diffraction a UV-Vis Spectroscopy. Unexpectedly, pure silica MFI zeolite exhibited the highest photocatalytic performance. Our findings demonstrated that large number of isolated silanol groups and silanol nests increase the formation of $^{\bullet}OH$, and enhance the productivity of oxygenate compounds and C_2H_6, while the Zn incorporated into the zeolite framework or attached to the silanol nests of the nanosized zeolites are less efficient. A mechanism of photocatalytic methane oxidation is proposed. These findings provide insights into the development of active nanosized zeolite photocatalysts with an extended amount of surface hydroxyl groups that can play a key role in photocatalytic methane conversion.

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THEME

☐ Theme 1 : Synthesis and shaping
☒ Theme 2: Applications for the environment, energy, and health
☐ Theme 3 : Characterization and modeling

Application of hybrid TiO_2/ZSM-5 zeolite photocatalysts in the photocatalytic treatment of industrial pesticide effluents

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Pesticides from agricultural runoff and industrial effluents contribute to water pollution due to their persistence, toxicity, and potential health risks. Conventional treatment methods often fail to remove these compounds efficiently, requiring more advanced approaches [1]. TiO_2/zeolite hybrid photocatalysts have emerged as promising materials for removing organic pollutants from aqueous environments due to their combined photocatalytic and adsorption properties [2]. The synergy of TiO_2 and zeolite enhances pollutant removal while facilitating easier recovery and reuse [3,4].

The aim of this study was to synthesize and evaluate the efficiency of TiO_2/ZSM-5 zeolite hybrid photocatalysts for the removal of herbicide clomazone (CLO) from aqueous solution and a pesticides' mixture (CLO, terbuthylazine, metamitron, metribuzin, bentazon, metalaxyl, haloxyfop-methyl, mefenpyr-diethyl, and dithiocarbamates) from industrial wastewater collected from pesticide company Agrosava d.o.o., Belgrade, Serbia. TiO_2/ZSM-5 zeolite hybrid photocatalysts were synthesized using the ultrasound solid-state dispersion method by combining ZSM-5 zeolite (Si/Al = 40) with two types of TiO_2 (20 wt% loading): commercial TiO_2 P25 nanoparticles (synthesized material: P25-ZSM5) and mixed shaped TiO_2 nanocrystals formed through thermal treatment of TiO_2 nanotubes (TNT-ZSM5). The characterisation of hybrid materials using XRPD, FTIR, and UV-Vis DR spectroscopy, as well as low-temperature nitrogen adsorption confirmed successful immobilization of TiO_2 while conserving the zeolite structure and TiO_2 optical properties. Additionally, TiO_2 deposition led to a reduction in the specific surface area of TiO_2/ZSM-5 hybrid photocatalysts compared to ZSM-5 zeolite. Under simulated solar irradiation, complete degradation of CLO in aqueous solution, detected by GC-MS analysis, was achieved in the presence of P25-ZSM5 after 60 min, while 96.4% removal was observed in the presence of TNT-ZSM5. After 180 min of irradiation, CLO removal from industrial wastewater reached 87.5% with P25-ZSM5 and 53.0% with TNT-ZSM5, while the overall pesticide removal was 86.7% for P25-ZSM5 and 68.6% for TNT-ZSM5. These results highlight the potential of TiO_2/ZSM-5 zeolite hybrid photocatalysts as efficient and practical materials for wastewater treatment.

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POSTERS
THEME 3

THEME

☐ Theme 1 : Synthesis and shaping
☐ Theme 2: Applications for the environment, energy, and health
☒ Theme 3 : Characterization and modeling

Machine Learning Perturbation Theory for an accurate prediction of adsorption enthalpies and activation energies in zeolites

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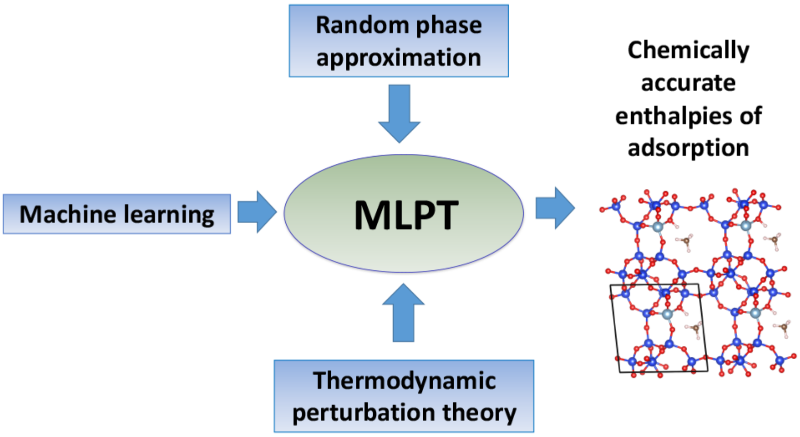
In an effort to further improve the accuracy of ab initio simulations and reach the chemical accuracy at a moderate computing cost, we propose a method that couples machine learning techniques with thermodynamic perturbation theory to estimate finite-temperature properties using correlated approximations [1-3]. We apply the MLPT approach to compute the enthalpies of adsorption of CO_2 and CH_4 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 or the Couple-Cluster levels of theory, which are among the most accurate quantum methods available today [3-5]. For the first time, we also report MLPT calculations of the free energies of activation of cracking and isomerization reactions of alkenes in protonated chabazite that combine several different electronic structure methods with molecular dynamics simulations [2]. We demonstrate that the use of a high level of theory (here Random Phase Approximation—RPA) is necessary to bridge the gap between experimental [6] and computed values [2]. In close connection with experiments, this theoretical methodology opens the path to an integrated approach for the development of optimized nanoporous materials in the fields of adsorption and catalysis.



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THEME

☐ Theme 1 : Synthesis and shaping

☐ Theme 2: Applications for the environment, energy, and health

☒ Theme 3 : Characterization and modeling

Real time tracking of Gallium oxides in MFI zeolites during pretreatment by infrared operando

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Introduction

Due to increasingly stringent environment protection laws and regulations, traditional fuel vehicles are being replaced by electric vehicles, resulting in a decline of the demand for gasoline and diesel in the transportation sector. The International Energy Agency forecast pointed out that from 2021 to 2030, more than one-third of the oil demand will be covered by the chemical products, and by 2050 this proportion will exceed 50% [1]. Since light olefins (ethylene and propylene) and BTXs (benzene, toluene and xylenes) are widely used as raw resources in all spheres of daily life, the petrochemical industry is now inclined to convert from « fuel type » production to « chemical type » production [2]. Nowadays, the production of high value-added chemicals (HVC) is limited to two technologies: catalytic reforming and steam cracking of naphta. Among alternative technologies, propane aromatization stands out for its commercial potential, with significant hydrogen co-production as an added economic benefit ($2C_3H_8 \leftrightharpoons C_6H_6 + 5H_2$). Gallium-doped zeolites represent a promising class of catalysts for this process, owing to their ability to facilitate the conversion of propane into aromatics.

The mobility of gallium species within the micropores of zeolites is a distinctive characteristic that significantly impacts their behavior. Specifically, the migration of gallium oxides is influenced by both temperature and the surrounding gas atmosphere. For instance, when gallium oxide is combined with a zeolite, Ga_2O_3 is reduced to Ga_2O in a hydrogen atmosphere [3]. Consequently, this reduced form can migrate within the zeolite to Brønsted acid sites, where it reacts to form active sites. These active sites, which are essential for propane transformation, are generated during the pretreatment process. Notably, this process can vary in complexity, ranging from a straightforward H_2 atmosphere to more intricate alternating environments, such as $H_2/O_2/H_2$ [4]. Importantly, an alternating pretreatment method leads to a more active catalyst. Therefore, determining the diffusion coefficient of gallium oxides within the zeolite is crucial for improving the design of more efficient catalysts.

To address this operando technique Fourier-Transform Infrared Spectroscopy (FTIR) is employed in this study. This state-of-the-art method enable the investigation chemical transformations occurring in gallium-doped zeolites under dynamic pretreatment conditions. We aim to elucidate the diffusion and kinetic mechanisms of gallium species within the zeolite pores. Furthermore, the study provides critical insights into the benefits of alternating pretreatment methods, such as $H_2/O_2/H_2$, for enhancing catalyst performance.

Materials and Method

A commercial ZSM-5 zeolite supplied by Zeolyst, with a Si/Al ratio of 43, was mixed with 5 wt% Ga and subjected to pretreatment at 530°C either an H_2 flow or successive steps of $H_2/O_2/H_2$. Operando FTIR experiments were also performed across the same temperature range, utilizing a specialized IR reactor cell, known as the "sandwich" cell, specifically designed for high-temperature operations.

Results and Discussion

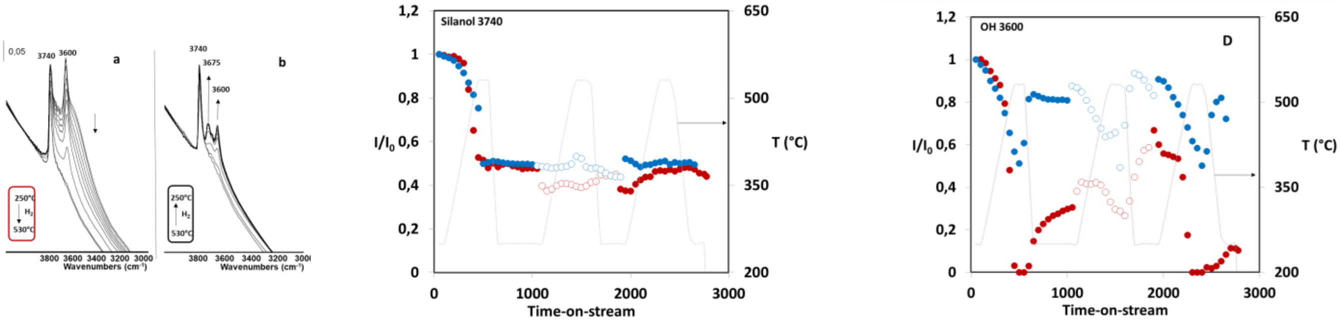

Figure 1: Infrared spectra of the Ga+ZSM-5 catalyst during the reductive pretreatment process, showing (a) the heating phase and (b) the cooling phase. Relative evolution of the silanol (c) and bridged OH (d) bands as a function of time on stream under different atmospheres (O_2 open symbol, H_2 full symbol), comparing the zeolite with and without gallium oxide.

Figures 1a-b show the infrared spectra of the bifunctional catalyst during reductive pretreatment. As the temperature increases, the silanol band (3740 cm^{-1}) partially decreases, while the 3600 cm^{-1} band, corresponding to bridged hydroxyl groups (Brønsted acid sites, BAS), completely disappears at high temperature, indicating a reaction with gallium oxide. During the cooling phase (Figure 1b), a portion of the Brønsted acid sites reappears, accompanied by the emergence of a new band at 3675 cm^{-1}, attributed to hydroxylated gallium Lewis acid sites.

Figures 1c-1d compare the temporal evolution of two specific bands—silanol and bridged hydroxyl groups—on the zeolite and the mechanical mixture under successive atmospheres ($H_2/O_2/H_2$). The loss of silanol intensity is attributed solely to thermal effects and is independent of the gas type. In contrast, the evolution of Brønsted acid sites (BAS) strongly depends on the gas atmosphere. Under H_2 at high temperatures, the bridged OH groups are completely consumed, but partial recovery occurs upon cooling. In the presence of O_2, a larger portion of BAS reappears, while a subsequent reduction step leads to a higher, irreversible incorporation of gallium species.

These observations indicate that gallium oxide species are mobile, with their mobility influenced by the gas atmosphere. Notably, the alternating gas pretreatment enhances the incorporation of gallium species, as supported by catalytic tests, which show higher activity for the mechanical mixture pretreated through successive gas steps.

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THEME

☐ Thème 1 : Elaboration et mise en forme de matériaux poreux

☐ Thème 2 : Applications pour environnement, énergie et santé

☒ Thème 3 : Modélisation et caractérisation de matériaux poreux

The impact of templates on the properties of porous materials

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The first zeolite synthesis using an organic template was done by Barrer and co-workers who obtained zeolite A using tetramethylammonium (TMA^+), the approach was later extended to low Si/Al ratio Beta (BEA) and Mobil Five (MFI) structures using tetraethylammonium (TEA^+) and tetrapropylammonium (TPA^+) respectively [1-3]. Since, several works have explored templates in zeolites trying to understand how organic molecules were driving the zeolites crystallization pathways [4]. The size and shape, the hydrophobicity, and the flexibility are the most important considered factors for templates [5]. Then, a wide variety of interactions were identified as main players behind the structuring phenomena i.e. Van Der Waals, hydrogen bonds and Coulomb electrostatic interactions [6, 7]. Templates were also used to synthesize aluminophosphates ($AlPO_4$) porous structures [8, 9], leading us to wonder about the interactions that occur between the $AlPO_4$ frameworks expected to be neutral and the charged organic templates. Furthermore, being efficient water sorbents with high capacities and low recycling energy, fundamental understanding of template-framework interactions may drive the enhancement of the properties of AlPOs answering current and foreseen water challenges [10]. In this contribution, we will show the investigation of both AFI zeotypes and MFI zeolites using advanced characterization techniques in both short- and long-range. The atomic ordering and final properties are revealed, shedding the light on the role of templates in controlling the properties of porous materials [11, 12].

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Acknowledgments

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THEME

☐ Theme 1 : Synthesis and shaping

☐ Theme 2 : Applications for the environment, energy, and health

☒ Theme 3 : Characterization and modeling

The Potential Relevance of n-hexane Cracking in the Characterization of Composite Zeolitic Materials

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Introduction

Zeolitic materials are extensively utilized in catalytic and separation-adsorption processes due to their high activity and exceptional selectivity. However, their application is restricted by narrow porosity, which limits their efficiency in the transformation and separation of bulkier molecules. To address this limitation, composite zeolites with hierarchical porosity have been developed. These hybrid materials combine the intrinsic properties of two distinct structures and benefit from enhanced diffusion capabilities provided by hierarchization, making them more versatile catalysts suitable for a broader range of applications. Characterization of such complex materials using conventional physicochemical techniques poses challenges, as these methods often fail to directly assess the reactivity of acid sites and, consequently, their catalytic properties. This gap can be bridged by employing model reactions.

One of the most commonly used catalytic tests is n-hexane cracking, a reaction initially introduced by the Mobil company in the 1960s and still widely applied under the term "α-test" [1]. This reaction proceeds via either monomolecular or bimolecular cracking mechanisms. The rate of monomolecular cracking is particularly sensitive to the strength of Brønsted acid sites (BAS) [2]. The strength of these sites is closely linked to their local environment, which includes the zeolite's structural and compositional framework, the precise location of acid sites within the framework, and the presence of extra-framework species [3]. Consequently, this catalytic test serves as a powerful tool to probe the acidic properties of composite zeolites. It provides valuable insights into the reactivity of these hybrid materials and reveals potential synergistic, additive, or intimacy effects within the hierarchical structures.

Materials and Methods

The transformation of n-hexane was conducted in a four-parallel fixed-bed reactor system. To ensure an accurate estimation of the reaction rate, the experiment was performed at four different contact times by varying the amounts of the same catalyst. The catalyst, with a particle size of 0.2–0.4 mm, was pre-treated at 540 °C under a nitrogen flow for 12 hours. A diluted n-hexane/nitrogen mixture was then injected into the reactors at 540 °C, maintaining a molar ratio of 11.

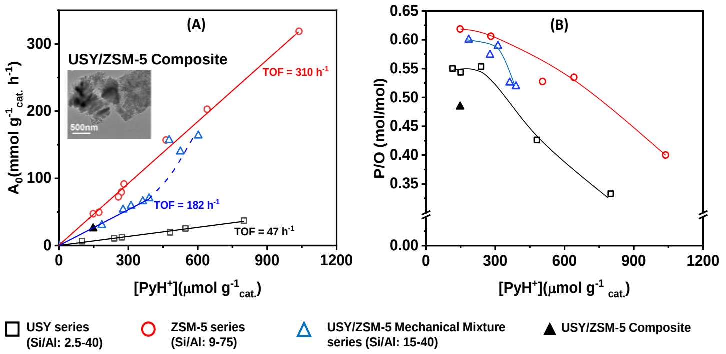

Figure 1. Variation of initial activity (A) and paraffins to olefins ration (B) as function of concentration of BAS probed by pyridine at 150 °C. A_0: initial activity of n-hexane cracking, P/O initial paraffins to olefins ratio.

Results and discussion

The catalytic activities of two series of catalysts USY, with a Si/Al ratio ranging from 2.5 to 40, and HZSM-5, with a Si/Al ratio from 9 to 75, are compared to those of USY/ZSM-5 mixtures (containing 41 % USY and 59 % of ZSM-5) and a composite with a USY/ZSM-5 ratio. The composite consists of hierarchical zeolite Y (41 wt. %) and nano-sized ZSM-5 (59 wt%), produced through partial interzeolite conversion from USY.

The activity is directly proportional to the number of BAS non-exalted by aluminum extraframework (Figure 1A). Accordingly, the turnover frequencies (TOF) of these sites are determined from the slopes of the linear plots of cracking activity versus the concentration of acid sites, measured by pyridine probing at 150 °C. The USY/ZSM-5 composite exhibits the same TOF as the series of mechanical mixtures with similar proportions but different concentrations of BAS (Figure 1A). Therefore, the activity of the composite materials corresponds to an algebraic sum of the activities of pure zeolite Y and ZSM-5. This indicates that the composite retains the distinct acidic properties of its individual components.

The paraffins-to-olefins ratio (P/O), calculated from initial reaction rates, is influenced by the zeolite framework but decreases notably with increasing BAS concentrations (Figure 1B) as a result of enhanced secondary cracking. At comparable BAS concentrations, the composite exhibits a significantly lower P/O ratio compared to the mechanical mixture, pure ZSM-5, or pure USY. This difference is likely due to the close interaction between the crystallites of the two zeolitic phases. The texture and intimate contact between these phases (as shown in the TEM image, Figure 1A) influence the balance between primary and secondary cracking, likely by improving the accessibility of acid sites.

Conclusion

The n-hexane cracking reaction (α-test) is demonstrated to be and remain a highly effective characterization tool for probing the catalytic properties of porous materials. Initial activity measurements reveal that the USY/ZSM-5 composite exhibits the intrinsic acidic characteristics of both USY and ZSM-5. Moreover, the interaction and proximity between the crystallites of the two structures significantly influence the material's selectivity. Consequently, this hybrid material displays promising catalytic properties, making it suitable for applications in the petroleum industry, fine chemical production, and the conversion of renewable resources.

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THEME

☐ Theme 1 : Synthesis and shaping

☐ Theme 2: Applications for the environment, energy, and health

☒ Theme 3 : Characterization and modeling

Formulating Flexible MOFs for Gas Separation

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Abstract

Metal-Organic Frameworks (MOFs) have emerged as a highly promising class of porous materials with a variety of potential applications, particularly in the field of separative adsorption. Indeed, MOFs exhibit suitable properties such as high surface area, molecule-sized pores, and can be easily tuned to adsorb specific molecules[1]. However, the synthesis of MOFs typically results in fine powder, which is a major drawback for industrial-scale applications due to its tendency to cause high pressure drop, clogging, and heat and mass transfer issues. In addition, the shaping of powder-based porous adsorbents facilitates their use in industrial processes, and generally improves their mechanical stability and abrasion resistance. However, a significant challenge remains: the shaped material must exhibit adsorption properties analogous to the original adsorbent powder. This requirement is even more challenging for flexible MOFs, which exhibit structure changes depending on the environmental conditions[2].

The goal of this work is to shape ZIF-8 and MIL-53 flexible MOFs in millimeter-sized extrudes while maintaining their flexibility. Different binder recipes were screened, using polymeric organic polyalcohol-based and cellulose-based binders. The shaped materials were compared based on the preservation of the textural properties and of their structural flexibility by nitrogen sorption (77 K), XRD and TGA. The addition of a binder is of interest in this case as his presence typically improves the mechanical properties of the shaped material. This aspect was investigated by compressibility tests. This work proposes binder recipes which allow the formulation of flexible MOFs, while retaining their breathing properties. The ultimate objective is to test these formulated materials for gas separation adsorption under mechanical stress.

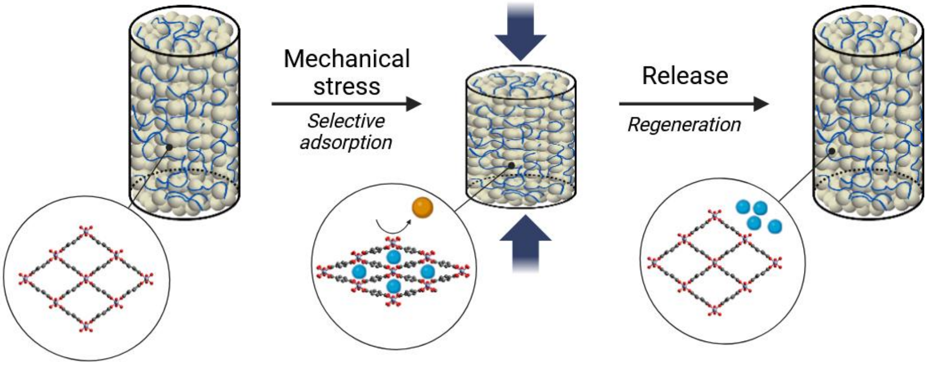

Fig. 1. Schematic representation of the concept: control of the breathing behavior of the flexible MIL-53 by applying a mechanical stress to induce a molecular-sieving type separation. In grey: MOF particles, in blue: binder.

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THEME

☐ Theme 1 : Synthesis and shaping
☐ Theme 2: Applications for the environment, energy, and health
☒ Theme 3 : Characterization and modeling

Separating CO_2 from H_2O: The performance of RHO nanozeolite

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The removal of CO_2 from the atmosphere and emission sources is inextricably linked to the presence of H_2O. While CO_2 possesses a high quadrupole moment and polarizability, the dipole moment of H_2O results in its preferential adsorption over CO_2 on solid adsorbents. To leverage the existing technological development of zeolites for CO_2 separation requires tolerating the presence of H_2O without significant detriment to the CO_2 separation performance. Recently, select examples of zeolites possessing eight-membered ring (8MR) structures have demonstrated enhanced CO_2 adsorption capacity in the presence of H_2O due to favourable adsorption environments.[1]

Here we explore the CO_2 adsorption behaviour of Na,Cs-RHO nanozeolite (Si/Al = 2) in the presence of H_2O with both equilibrium isotherm analysis and dynamic adsorption conditions using a combination thermogravimetric analysis (**Figure 1, left)**, *in situ* neutron scattering (**Figure 1, right)**, and breakthrough curve measurements. Due to the well-known flexibility of the RHO framework structure, different amounts of water adsorbed within the microporosity affect the distribution of the extra-framework cations and distortion of the 8MRs, influencing the diffusion of guest molecules.[2] By tuning the nanozeolite pre-treatment (vacuum, temperature), the CO_2 adsorption behaviour of Na,Cs-RHO nanozeolite responds with restricted CO_2 adsorption at high dehydration and rapid adsorption when higher amounts of H_2O are retained in the microporosity. This raises the question of whether small pore zeolites, possessing key structural features, can demonstrate the necessary performance and durability to facilitate the separation of CO_2 from H_2O.

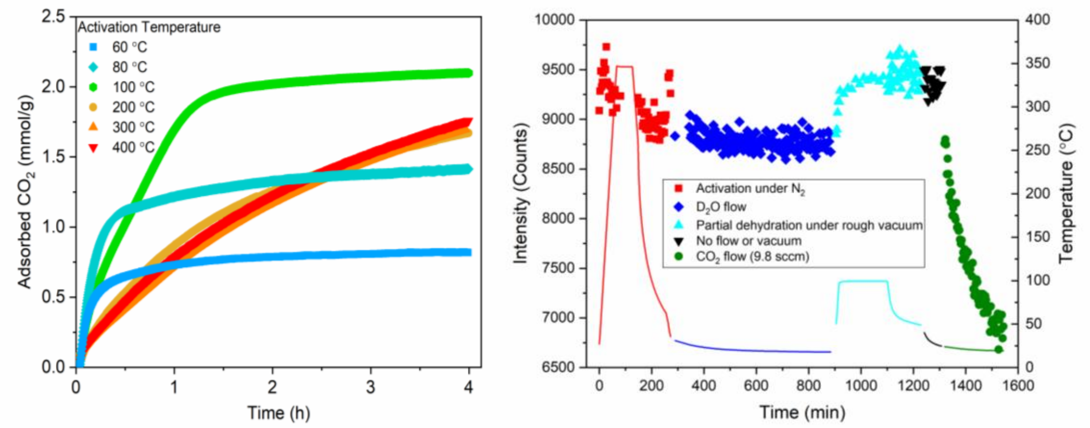

Figure 1. (left) CO_2 adsorption at 20 °C measured by TGA with different activation temperatures of the RHO nanozeolite, **(right)** neutron diffraction data showing the change in the peak intensity over time in response to dehydration, D_2O adsorption, and CO_2 adsorption.

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THEME

☐ Theme 1 : Synthesis and shaping
☐ Theme 2: Applications for the environment, energy, and health
☒ Theme 3 : Characterization and modeling

Study of the adsorption properties of radon and xenon in zeolites, a Grand Canonical Monte Carlo simulation study.

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The detection of rare events, such as dark matter and/or neutrino-less double beta decay, in the field of subatomic physics, employs ultra-sensitive detectors, usually based on a target of liquefied noble gases, such as xenon. Nevertheless, radon, a radioactive noble gas present within the target in trace amounts constitutes the main source of background and therefore needs to be removed. Microporous materials, such as zeolites or MOFs, has shown an interesting potential in separation of noble gases binary mixtures [1]. However, separating radon from xenon appears as particularly challenging, due to their similar atomic dimensions, in addition to their extremely limited reactivity.

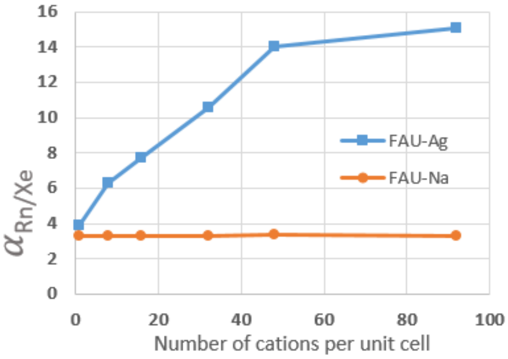
For that purpose, we have applied the Grand Canonical Monte Carlo (GCMC) technique to simulate radon and xenon adsorption properties, such as room temperature adsorption isotherms, the Henry constants and the adsorption heat evolution with loading, in order to optimize parameters of zeolites to selectively adsorb radon. This systematic study explored the influence of the Si/Al ratio, the chemical nature of the extra-framework cations, as well as their crystallographic positions. Moreover, to investigate the effect of the framework topology, three zeolites with differing largest pore openings were considered: FAU (12MR), FER (10MR), and LTA (8MR).

The observations revealed that although the Rn/Xe adsorption properties are influenced by the zeolite topology, the primary factors driving adsorption selectivity are the chemical nature of the cations, their concentration and accessibility. Consequently, as illustrated in Table 1, the adsorption properties of LTA zeolite are consistently superior to those of FAU structure. Nevertheless, as shown in Figure 1, increasing the amount of Ag^+ in accessible crystallographic sites, significantly enhances the adsorption properties, compared to Na^+ cations.

Table 1: Rn/Xe adsorption selectivity of FAU-(Na^+/Ag^+) and LTA-(Na^+/Ag^+) with Si/Al ratio = 1.

Si /Al =1	FAU		LTA	
$\alpha_{Rn/Xe}$	Ag^+	Na^+	Ag^+	Na^+
	14,8	3,2	22,2	4,3

Figure 1: Evolution of Rn/Xe adsorption selectivity in Ag-FAU and Na-FAU as a function of the number of cations per unit cell.



The authors acknowledge the financial support of the project ANR-23-CE31-0022 (IRENE).

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THEME

☐ Theme 1: Synthesis and shaping

☐ Theme 2: Applications for the environment, energy, and health

☒ Theme 3 : Characterization and modeling

Cation Distribution in Potassium-Exchanged Nano Y zeolite from 3D ED

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The chemical nature and distribution of charge compensating cations within zeolites significantly influence their physicochemical properties. However, the localization of these cations is often challenging due to the small size of zeolite crystals, restricting the application of techniques such as single-crystal X-ray diffraction. Similarly, the Rietveld method, although applicable in some cases, may prove difficult or even impossible for nanometer-sized crystals. The three-dimensional electron diffraction (3D ED) technique using a transmission electron microscope (TEM) allows to counter these issues. Moreover, applying precession on the electron beam significantly reduces the dynamic effects resulting from electron–matter interactions. [1].

Recently, we applied the 3D ED technique to nanometer-sized faujasite Y (Si/Al = 2.33), synthesized via the hydrothermal method [2]. Using this technique, and after exchange with K^+, the structure was solved in space group $Fd\bar{3}m$ (Fig. 1a) [3]. Fig. 1b illustrates the distribution of K^+ across positions I, I', and II in K-Y as determined by the dynamical structure refinement based on 3D ED data. The high vacuum within the TEM chamber (10^{-5} Pa) induced significant dehydration. After the final refinement cycle, fewer than one water molecule per sodalite cage was detected, and the supercages were completely empty. Despite this low water content, no short $K^+\cdots K^+$ contacts (resulting from simultaneous occupancy of site I and I') were observed, indicating the absence of cation crowding. The Si/Al ratio appears too high for such phenomena to occur; higher aluminum content is necessary to observe these effects [4]. Furthermore, Monte Carlo (MC) simulations describing the distribution of potassium cations across their crystallographic sites as a function of the number of adsorbed water molecules corroborated the crystallographic findings.

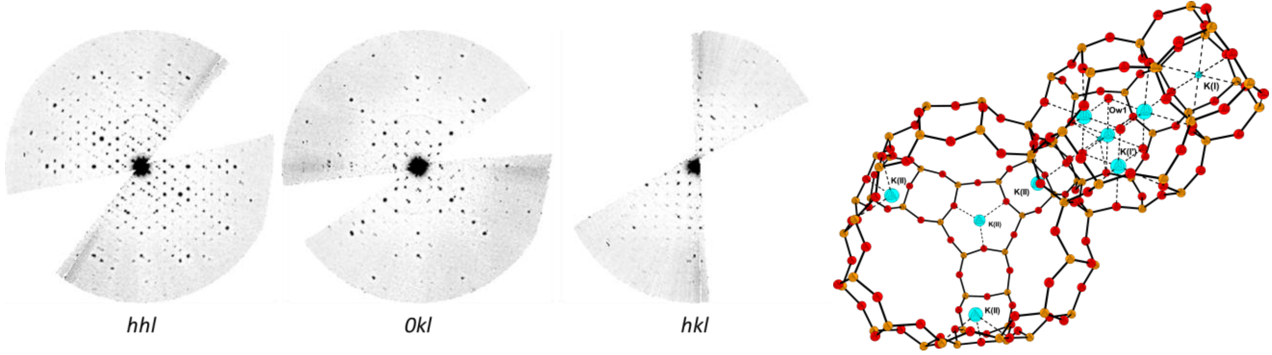

Fig.1. (a) Reconstructed reciprocal-space sections along three different directions confirming the reflection conditions of space group $Fd\bar{3}m$ (*hhl* : *h* + *l* = 2n; 0*kl* : *k* + *l* = 4n, and *k*,*l* = 2n, *hkl* : *h* + *k* = 2n and *h* + *l*, *k* + *l* = 2n) and (b) cation distribution (sites I, I' and II) in the K-Y zeolite framework determined by 3D ED.

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THEME

☐ Theme 1 : Synthesis and shaping

☐ Theme 2: Applications for the environment, energy, and health

☒ Theme 3 : Characterization and modeling

Influence Of The Water Loading Ratio On The Diffusion Of HTO Radiolysis Products H_2, O_2 And H_2O_2 In Zeolite 4A Using Ab Initio Molecular Dynamics

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When tritiated water is stored in containers containing zeolite 4A pellets as adsorbate, the production of gaseous species H_2 and O_2 induced by self-radiolysis displays a complex behavior [1]. In a first stage, it is accelerated compared to the production rate in free water. This "catalytic stage" induced by the Z4A is then followed by a "recombination stage" during which a large decrease is observed until the total disappearance of the two molecular species in the gas phase. The duration characterizing each stage depends on many factors, among which the initial water loading ratio of Z4A pellets. Recombination was only observed for water loading ratios below around 13%. Below this threshold, the lower the loading, the earlier recombination happens. In order to explore this unusual recombination of H_2 and O_2 into H_2O, a numerical investigation using density functional theory as implemented in the CP2K package was conducted. Ab initio molecular dynamics simulations were performed for various mixtures of those molecules, and for different water loading ratios. In addition, similar simulations were performed for hydrogen peroxide, another stable product of water radiolysis. The obtained trajectories were used to compute and compare mean squared displacements and diffusion coefficients to provide insight into the kinetics of the species in a zeolite K4 unit cell, which is a common, smaller substitution lattice for the Z4A unit cell. Water and hydrogen peroxide are rapidly chemisorbed onto the 8R cationic site, while dioxygen and furthermore dihydrogen, remain mobile. These results help in identifying the most probable encounters, in turn suggesting a likely reaction path. In addition, these trajectories provide information on the rate of small timescale events, such as intersite diffusion.

Recently, classical molecular dynamics simulations were started in order to explore the diffusion of the radiolysis products on longer timescales. These trajectories will provide information on the rates of diffusion between cages. The ab initio and classical trajectories thus provide complementary rates for different types of diffusion events inside the zeolite, depending on their timescale. Combined with rates of the main reactions involved in water radiolysis [2], a kinetic Monte Carlo (KMC) program will then be developed to include all events susceptible of playing a role in the recombination process. This program will simulate the full duration of the recombination, on the order of a few hundred days for the highest loading rates ratios.

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THEME

☐ Theme 1 : Synthesis and shaping

☐ Theme 2: Applications for the environment, energy, and health

☒ Theme 3 : Characterization and modeling

Identification of zeolite BEA polymorphs by solid-state ^{29}Si NMR Spectroscopy

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Beta (BEA) zeolite is among the most prevalent zeolites, characterized by a complex polymorphic structure [1]. The precise determination of the structural composition of the individual polymorphs, and their contribution to the overall structure of intergrown zeolitic materials is supposed to improve the comprehension of their physicochemical and catalytic properties.

Here, we report the analysis of individual polymorph structures in pure-silica BEA zeolite using solid-state ^{29}Si NMR spectroscopy[2].

To identify the signals in ^{29}Si MAS NMR spectra of pure-silica BEA zeolite, we used the specially developed homonuclear decoupled CT-INADEQUATE-CR MAS NMR pulse sequence, which demonstrates improved resolution (down to 0.1 ppm) and the sensitivity for zeolites and silicate materials. This sequence was applied to pure-silica zeolite BEA enriched with 25% ^{29}Si and synthesized by hydrothermal synthesis in fluoride media.

This technique allows for the resolution and identification of two signal subsystems, nine lines per each. They correspond to silicon atoms situated in non-equivalent T-sites of A and B polymorphs of BEA (fig.1a). The obtained assignment makes possible the reconstruction of individual ^{29}Si MAS NMR spectra for each A, B and C BEA polymorph (fig.1b).

According to the obtained results, the analytical protocol for quantitatively identifying the polymorph composition of high-silica crystalline BEA zeolites (Si/Me > 100) by corresponding deconvolution analysis of their 1D ^{29}Si MAS NMR spectra was suggested (fig.1c).

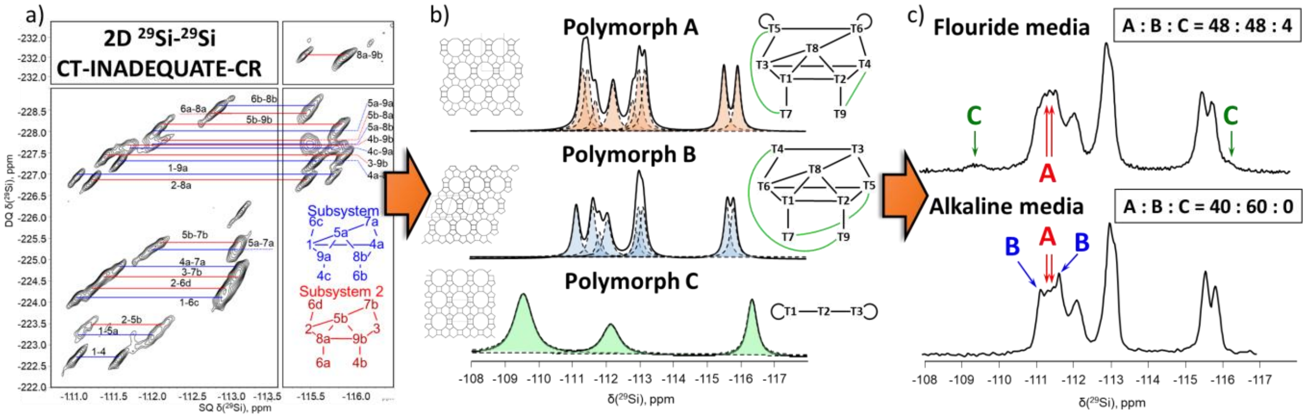

Fig. 1. (a) 2D ^{29}Si INADEQUATE-CR of ^{29}Si-enriched Si-BEA zeolite, (b) extracted 1D ^{29}Si MAS NMR spectra of A, B and C polymorphs, (c) 1D ^{29}Si MAS NMR spectra of Si-BEA synthesised in different media.

References

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THEME

☐ Theme 1 : Synthesis and shaping
☐ Theme 2: Applications for the environment, energy, and health
☐ Theme 3 : Characterization and modeling

Characterizing Biochar through Gas Adsorption: Surface Area, Pore Size Distribution, and Sorption Energy

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Biochar, a carbon-rich substance derived from biowastes via pyrolysis, has gained attention for its promising potential due to its distinctive structural features, including a high surface area, porosity, and adjustable surface chemistry. These characteristics make it ideal for various environmental uses, such as carbon storage, water treatment, and serving as a catalyst support. However, precisely characterizing biochar's adsorption properties is challenging because of its complex and varied structure [1]. This study examines the surface properties of biochar through gas adsorption methods, specifically focusing on CO_2 , N_2 , and water vapor adsorption. The goal is to assess important factors like surface area, pore size distribution, and sorption energy. The adsorption isotherms gathered allow for a comparison of the material's performance under different conditions, providing a deeper understanding of its adsorption behavior. The findings offer valuable insights into the structure-adsorption relationship of biochar, contributing to the advancement of more efficient applications in both environmental and industrial sectors.

References

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GENERAL ASSEMBLY

Thursday, April 3rd, 2025, at 10:15 am

After the renewal of the members of the GFZ board by the General Assembly of the association held on March 29th, 2024, in La Rochelle, the number of people sitting on the GFZ board was nine in accordance with the statutes of the association.

Composition of the board:
- Benoît Louis (President), ICPEES – Strasbourg
- Christophe Bouchy (Secretary), IFPEN – Solaize
- Emily Bloch (Treasurer), Madirel – UMR 7246 – Marseille
- Alexandre Legrand (Member), UCCS – Lille
- Rémy Guillet-Nicolas (Member) LCS – UMR 6506 – Caen
- Louwanda Lakiss (Member), LCS – UMR 6506 – Caen
- Alexander Sachse (Member), IC2MP – Poitiers
- Andrey Ryzhikov (Member), UHA – Mulhouse
- Julien Grand (Member, substitute S. Van Daele), TotalEnergies – Feluy

The assembly will be asked to replace or renew three members of the board:
- Benoît Louis (President), ICPEES – Strasbourg
- Christophe Bouchy (Secretary), IFPEN – Solaize
- Alexander Sachse (Member), IC2MP – Poitiers

To replace these outgoing members, the board will receive applications at the GFZ meeting. These applications will be put to a vote during the General Assembly. Candidates are asked to make themselves known to a member of the board before Wednesday April 2nd, 6 p.m.

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