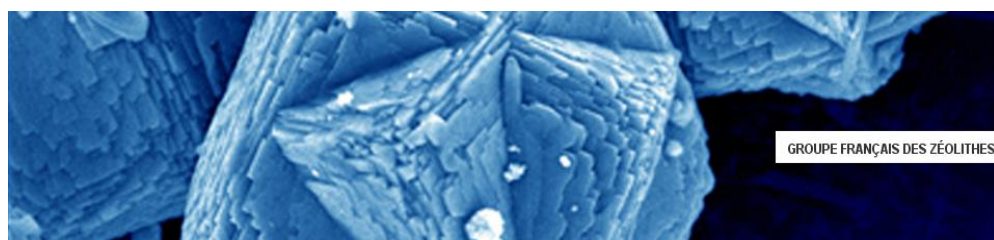


**GFZ 2024**



# PROGRAMME



***39<sup>ème</sup> réunion annuelle du GFZ du 26 mars au 29 mars 2024, précédée d'une école thématique les 25 et 26 mars 2024, à la résidence Club La Fayette à La Rochelle***

**Lundi 25 mars**

**Mardi 26 mars**

**Mercredi 27 mars**

**Judi 28 mars**

**Vendredi 29 mars**

08h30	
09h45	Pause
10h00	
11h15	Pause
11h30	
12h45	Déjeuner
14h15	Quartier libre
15h30	Navette depuis La Rochelle
16h30	Accueil des participants à l'école d'été et café de bienvenue
17h00	J. Daou: zeolites: synthesis, applications and shaping
18h15	Pause
18h30	D. Curulla: Design of Experiments and Machine Learning: the best of the two worlds
20h00	Apéritif de bienvenue
20h30	Dîner

08h30	J.P. Gilson: applications des zéolithes: leçons du passé et regard vers l'avenir
09h45	Pause
10h00	C. Volklinger: les MOFs appliqués au nucléaire
11h15	Pause
11h30	R. Denoyel: caractérisation des matériaux par adsorption
12h45	Déjeuner
14h15	Quartier libre
16h30	Accueil des participants à la réunion annuelle GFZ et installation poster
17h00	Cérémonie d'ouverture
17h15	Plénière P. Poinot
18h00	Session exposants
18h30	Quartier libre
19h30	Apéritif de bienvenue
20h00	Dîner

09h00	Plénière S. Baudron
09h45	O1.1. P. Hardy O1.2. L. Pace O1.3. J. Wu
10h30	Pause
11h00	O1.4. T. Gaillard O1.5. C. Got O1.6. T. Devic O1.7. A. Fateeva
12h15	Déjeuner
13h45	Keynote I. Batonneau-Gener
14h15	Session flashes
15h00	Session poster
16h00	Pause
16h30	Aquarium sponsorisé Anton Paar
20h00	Dîner

09h00	Plénière L. Pinard
09h45	O2.1. H. Zhao O2.2. M. El Zayed O2.3. L. Premet
10h30	Pause
11h00	O2.4. D. Andriotou O2.5. L. Mussard O2.6. M. Hureau O2.7 C. Longue
12h15	Déjeuner
13h45	Plénière C. Miqueu
14h30	O3.1. Y.M. Chaib Draa O3.2. N. Abidi
15h00	Session poster
16h15	Pause
16h30	Workshop: present your scientific poster with impact
18h45	Dégustation Pineau sponsorisée 2S Instrument
20h00	Banquet
22h00	soirée dansante

09h00	O3.3. M. Castella Ventura O3.4. E. Clatworthy
09h30	Pause
09h45	AG et remise des prix
12h00	Clôture de la réunion
12h30	Navette pour La Rochelle

## 39<sup>ème</sup> réunion du GFZ 2024

Programme Scientifique de la réunion annuelle	
<i>Mardi 26 mars 2024 après midi</i>	
<b>16h30</b>	Accueil des participants et installation des posters
<b>17h00</b>	Ouverture du congrès
<b>Chairmen: Benoît Louis et Alexander Sachse</b>	
<b>17h15</b>	<b>Conférence plénière:</b> "Induced-volatolomics, a new research field in chemistry" <b>Pauline Poinot</b> (IC2MP)
<b>18h00</b>	<b>Présentations Exposants</b>
<b>EXP-1</b>	<b><i>Présentation de la société Bruker</i></b> <i>D. Cochet</i>
<b>EXP-2</b>	<b><i>Présentation de la société Courtage Analyses Services / 2S-Instruments</i></b> <i>S. Sigrist</i>
<b>EXP-3</b>	<b><i>Présentation de la société Ribori instrumentation</i></b> <i>M. Faryssy</i>
<b>EXP-4</b>	<b><i>Présentation de la société Anton Paar</i></b> <i>D. Bourgeois</i>
<b>EXP-5</b>	<b><i>Présentation de la société Micromeritics</i></b> <i>P. Szitas</i>
<b>18h30</b>	Quartier libre
<b>19h30</b>	<i>Apéritif de bienvenue et dîner</i>

Mercredi 27 mars 2024

Chairmen: Benoît Louis et Alexandre Legrand

09h00	<b>Conférence plénière:</b> "Deep eutectic solvents as media for MOF synthesis" <b>Stéphane Baudron</b> (Unistra)
09h45	<b>Oral 1 Thème 1:</b> <b>P. Hardy</b> , M. Taieb Bakouche, M. Ferreira, C. Campagne, T. Loiseau, F. Pourpoint, J. Dhainaut, C. Volkringer: "Facile synthesis of Zr-MOF/polyester composites for the degradation of nerve agents"
10h00	<b>Oral 2 Thème 1:</b> <b>L. Pace</b> , E. Dib, S. Mintova: "The impact of templates on the local order and properties of aluminophosphate"
10h15	<b>Oral 3 Thème 1:</b> <b>J. Wu</b> , Q. Yue, S. Mintova: "Morphology control of ZSM-11 zeolite using novel templates and additives"
10h30	<i>Pause</i>
<b>Chair(wo)men: Louwanda Lakiss et Stéphane Baudron</b>	
11h00	<b>Oral 4 Thème 1:</b> <b>T. Gaillard</b> , T. Aubert, A. Galarneau: "Manufacturing of zeolite monoliths through pseudomorphic transformation of 3D printed mesoporous silica monolith"
11h15	<b>Oral 5 Thème 1:</b> <b>C. Got</b> , A. Tuel, B. Harbuzaru: "Synthèse de Chabazite cœur-couche possédant une surface hautement silicique"
11h30	<b>Oral 6 Thème 1:</b> N. Gedikoglu, M. Paris, N. Guillou, C. Martineau, G. Mouchaham, N. Heymans, G. de Weireld, A. Fateeva, E. Bloch, S. Bourrelly, J. Ostolaza-Paraiso, D. Fairen-Jimenez, <b>T. Devic</b> : "Is there any benefit of using the gallate complexing group to prepare new MOFs: the key impact of residual phenolic protons"
11h45	<b>Oral 7 Thème 1:</b> B. Gikonyo, F. Liu, S. De, C. Journet, C. Marichy, <b>A. Fateeva</b> : "MOF thin films growth by Atomic/Molecular Layer Deposition"
12h15	<i>Déjeuner</i>

Chairmen: Alexander Sachse / Andrey Ryzhikov

13h45	<b>Keynote:</b> "Radicals in Zeolites" <b>Isabelle Batonneau-Gener</b> (IC2MP)
14h15	<b>Présentations flash Thème 1 (Synthèse et mise en forme), Thème 2 (Applications pour l'environnement, l'énergie et la santé) et Thème 3 (Caractérisation et modélisation)</b>
<b>P1-1</b>	<b>OSDA-free synthesis of ZSM-5 nanosheets with short b-thickness</b> Q. Yue, H. Liu, Z. Qin, S. Mintova
<b>P1-2</b>	<b>Synthesis of Faujasite from natural clay via high-pressure hydrothermal method</b> S.B. Gambo, N.P. Martin, C. Chassigneux, N. Dairou, V. Wernert

<b>P1-3</b>	<b>In situ transformation of layered double hydroxide arrays into 2D Metal Organic Framework for oxygen evolution reaction</b> Y. Smati, M. Turmine, V. Vivier, <u>J. Reboul</u> , J. Blanchard
<b>P1-4</b>	<b>Synthesis of ZSM-5 from Si residues of solar panel production</b> R.S.R. Oliveira, <u>L. Bieseki</u> , S.B.C. Pergher
<b>P1-5</b>	<b>Elaboration de matériaux composites MOF A520/polymères pour l'adsorption de l'humidité ambiante</b> <u>M. Froehly</u> , G. Chaplais, H. Nouali, V. Roucoules, P. Forler, T.J. Daou
<b>P2-1</b>	<b>Metal-Organic Frameworks: Evaluating cytotoxicity assays and their antiviral activity against coronaviruses</b> <u>O.-E. Plastiras</u> , P. Bouquet, J. Dhainaut, J.-P. Dacquin, A. Goffard, C. Volkringer
<b>P2-2</b>	<b>Unconventional coke composition originating from anisole disproportionation on zeolites</b> <u>N. Pichot</u> , N. Chaouati, Y. Pouilloux, A. Dufour, L. Pinard
<b>P2-3</b>	<b>Enhancing the efficiency of CO<sub>2</sub> removal by reducing the size of zeolite crystals</b> <u>S. Ghojavand</u> , E. Clatworthy, R. Guillet-Nicolas, B. Coasne, V. Pugnet, P. Kumar-Gandhic, S. Mintova
<b>P2-4</b>	<b>Zéolithes modifiées par les nanoparticules de Fe et de Ni comme catalyseurs efficaces pour la réduction catalytique de polluants organiques</b> A. Mekki, <u>R. Hamacha</u> , A. Mokhtar, M. Hachemaoui, H. Habib Zahmani, S. Hacini, B. Boukoussa
<b>P2-5</b>	<b>Shaped MOF composites: promising materials in CCUS technology</b> <u>Y. Khadiri</u> , A. Anouar, S. Royer, A. El Kadib, T. Loiseau, J. Dhainaut
<b>P3-1</b>	<b>Mesure de coefficients de diffusion de l'eau dans des matériaux poreux par PFG <sup>1</sup>H NMR</b> <u>F. Bihl</u> , B. Vincent, A-C. Roger, B. Louis
<b>P3-2</b>	<b>Influence of ligands on position and coordination of cobalt cations in FAU zeolite</b> <u>G. Medak</u> , F. Dalena, D. Kuzman, M. Cindrić, S. Mintova
<b>15h00</b>	Session poster / <i>Pause</i>
<b>16h30</b>	<i>Visite de l'aquarium de La Rochelle sponsorisée par Anton Paar</i>
<b>20h00</b>	<i>Dîner</i>

Jeudi 28 mars 2024

**Chairmen: Christophe Bouchy et Rémy Guillet-Nicolas**

<b>09h00</b>	<b>Conférence plénière:</b> "" <b>Ludovic Pinard</b> (LCS)
<b>09h45</b>	<b>Oral 1 Thème 2: H. Zhao</b> , X. Yang, R. Guillet-Nicolas, V. Yasnou, V. Valtchev: "Microporous materials for energy-saving atmospheric water harvest"
<b>10h00</b>	<b>Oral 2 Thème 2: M. El Zayed</b> , P. Bazin, F. Dalena, R. Zhang, L. Pinard: "Positive effects of controlled nanoconfined metals for LOHC regeneration"
<b>10h15</b>	<b>Oral 3 Thème 2: L. Premet</b> , E. Oheix, G. Chaplais, L. Pieuchot, T.J. Daou: "Films composites antibactériens à base de MOF ZIF-8/ZIF-dia(Zn)"
<b>10h30</b>	<i>Pause</i>
<b>Chairmen: Stijn Van Daele et Stéphane Lecarpentier</b>	
<b>11h00</b>	<b>Oral 4 Thème 2: D. Andriotou</b> , G. Frajer, A. Roussey, E. Billy, D. Peralta: "Innovative approaches for recycling old batteries solution through the precipitation of ZIFs"
<b>11h15</b>	<b>Oral 5 Thème 2: L. Mussard</b> , I. Batonneau-Gener, P. Moreau: "Purification des huiles de pyrolyse par adsorption sur des zéolithes modifiées"
<b>11h30</b>	<b>Oral 6 Thème 2:</b> P.H. Morais Andrade, C. Volkringer, T. Loiseau, H. Vezin, <b>M. Hureau</b> , A. Moissette: "Charge Transfer Complexes between Gaseous Iodine and MOF Materials: Exploring Dynamics and Reactivity"
<b>11h45</b>	<b>Oral 7 Thème 2: C. Longue</b> , Y. Zhang, Q. Zheng, R. Bingre, C.G. Flores, A.V. Silva, M.M. Pereira, L. Pinard, B. Louis: "How does a bottom-up approach using biomass for the synthesis of hierarchical ZSM-5 zeolites affect the MTO reaction?"
<b>12h15</b>	<i>Déjeuner</i>

**Chairm(wo)men: Emily Bloch et Benjamin Claessens**

<b>13h45</b>	<b>Conférence plénière:</b> "Modeling gas adsorption in zeolites, taking into account different adsorption mechanisms" <b>Christelle Miqueu</b> (LFCR)
<b>14h30</b>	<b>Oral 1 Thème 3: Y.M. Chaib-Draa</b> , T. Ors, I. Déroche, J.L. Paillaud: "3D ED pour la localisation des cations dans des faujasites échangées"
<b>14h45</b>	<b>Oral 2 Thème 3: N. Abidi</b> , Y. Boudjema, C. Chizallet, K. Larmier: "Unveiling closed and open site stability of Sn-, Ti-, Hf-, and Zr-Beta zeolites: A DFT investigation for biomass sugar conversion"
<b>15h00</b>	Session poster / <i>Pause</i>
<b>16h30</b>	Workshop: present your scientific poster with impact
<b>18h45</b>	<i>Dégustation de Pineau sponsorisée par 2S Instrument</i>
<b>20h00</b>	<i>Banquet</i>
<b>22h00</b>	Soirée dansante

Vendredi 29 mars 2024

**Chair(wo)men: Christelle Miqueu et Rémy Guillet-Nicolas**

<b>09h00</b>	<b>Oral 3 Thème 3: M. Castellà-Ventura</b> , A. Moissette, E. Kassab: "Theoretical Study of the Steric Hindrance Effects on Pyridine Derivatives Adsorption in H-ZSM5 Zeolite"
<b>09h15</b>	<b>Oral 4 Thème 3: E.B. Clatworthy</b> , S. Moldovan, K. Nakouri, S.P. Gramatikov, F. Dalena, M. Daturi, P.St. Petkov, G.N. Vayssilov, S. Mintova: "Direct Visualisation of the Flexibility of RHO Nanozeolite"
<b>09h30</b>	<i>Pause</i>
<b>09h45</b>	<b>Assemblée Générale / Remise des prix jeune chercheur, thèse, oraux et posters / Renouvellement partiel du bureau du GFZ</b>
<b>12h00</b>	<b>Clôture de la réunion</b>
<b>12h30</b>	<b>Navette pour La Rochelle</b>

**PLENIERES**



# INDUCED-VOLATOLOMICS, A NEW RESEARCH FIELD IN CHEMICAL BIOLOGY

Pauline POINOT

University of Poitiers, UMR CNRS 7285, Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), 4 rue Michel-Brunet, TSA 51106, 86073 Poitiers cedex 9, France

Pauline.poinot@univ-poitiers.fr, <https://ic2mp.labo.univ-poitiers.fr/>

## Summary:

The volatolome corresponds to the whole volatile organic compounds (VOCs) produced by the metabolic activity of any biological system. A change in the volatolome can be linked to the development of a disease and its study, i.e. volatolomics, is a simple, fast, accessible, and safe diagnostic approach. However, the identification of endogenous volatile markers specific to a pathology is limited due to the high interindividual variability and the disparities between laboratories in sample preparation and analysis.

In this context, our multidisciplinary team has proposed a new paradigm, called Induced Volatolomics<sup>[1]</sup>, to explore biological processes in real time.

This strategy relies on the use of off-on VOC-based probes that can be converted into exogenous volatile compounds through a metabolic stimulus. The targeted enzymes can be linked to specific physiopathological processes as cancer, viral or bacterial infection, or inflammation processes.

In this presentation, the concept of off-on VOC-based probes will be presented. Their value for the in vivo diagnosis of tumors will be described. Also, their use to survey and improve the efficacy of novel chemotherapeutic agents will be demonstrated<sup>[2]</sup>. Then, a new concept relying on cocktails of VOC-based probes will be introduced. These novel chemobiological tools showed great advantages for the evaluation of multiple enzymes dysregulation in cancer or viral infection<sup>[3,4]</sup>. Pilot results implying these cocktails will be presented.

[1] F. Djago, J. Lange, P. Poinot, *Nature Reviews Chemistry* **2021**, *5*, 183–196.

[2] J. Lange, B. Eddhif, M. Tarighi, T. Garandeau, E. Péraudeau, J. Clarhaut, B. Renoux, S. Papot, P. Poinot, *Angew. Chem. Int. Ed.* **2019**, *58*, 17563–17566.

[3] R. Châtre, E. Blochouse, R. Eid, F. Djago, J. Lange, M. Tarighi, B. Renoux, J. Sobilo, A. Le Pape, J. Clarhaut, C. Geffroy, I. Opalinski, W. Tuo, S. Papot, P. Poinot, *Chem. Sci.* **2023**, *14*, 4697–4703.

[4] E. Blochouse, R. Eid, N. Araj, W. Tuo, R. Châtre, S. Papot, N. Lévêque, R. Thuillier, P. Poinot, *Anal. Chem.* **2023**, *95*, 11572–11577.



## 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

### Deep eutectic solvents as media for MOF synthesis

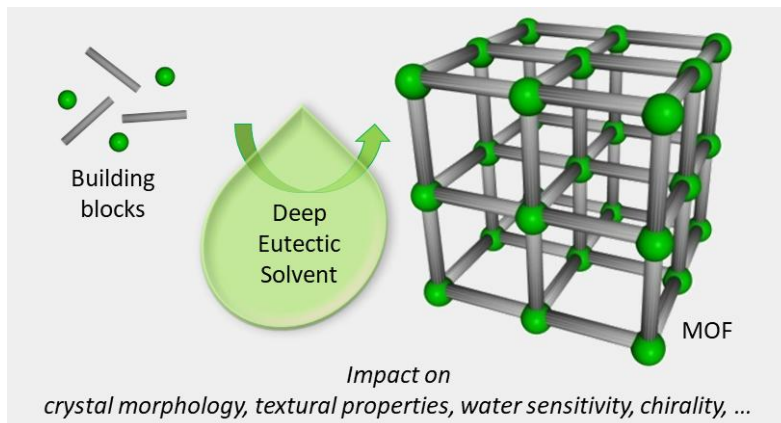
Stéphane A. Baudron,<sup>a</sup> Renata A. Maia,<sup>a</sup> Michaël Teixeira,<sup>a</sup> Pauline André,<sup>a</sup> Tracy El Achkar,<sup>a</sup> and Benoît Louis<sup>b</sup>

<sup>a</sup> UMR 7140, University of Strasbourg-CNRS, 4 rue Blaise Pascal, 67000 Strasbourg  
 e-mail: sbaudron@unistra.fr

<sup>b</sup> UMR 7515, ICPEES, University of Strasbourg-CNRS, 25 rue Becquerel, 67087 Strasbourg

Deep Eutectic Solvents (DESs) represent an emerging class of solvents featuring some characteristics of their ionic liquid cousins - low vapor pressure, relatively wide liquid range, non-flammability and the ability to dissolve polar species - along with unique specificities, such as their limited toxicity and an improved biocompatibility.<sup>1</sup> Their use as media for the preparation of Metal-Organic Frameworks (MOFs) has been recently explored, showing that not only DESs represent green and less toxic alternatives to solvents commonly used in the synthesis of these porous crystalline materials, but also that they may play different roles in the MOF construction.<sup>2</sup>

In this contribution, our recent efforts aiming at further investigating the potential of DESs for MOF synthesis will be presented.<sup>3-6</sup> In particular, their impact on the properties of the porous materials such as crystal morphology, textural properties,<sup>3-4</sup> water sensitivity<sup>5</sup> and chirality<sup>6</sup> will be discussed.



## References

1. B. B. Hansen, St. Spittle, B. Chen, D. Poe, Y. Zhang, J. M. Klein, A. Horton, L. Adhikari, T. Zelovich, B. W. Doherty, B. Gurkan, E. J. Maginn, A. Ragauskas, M. Dadmun, T. A. Zawodzinski, G. A. Baker, M. E. Tuckerman, R. F. Savinell, J. R. Sangoro, *Chem. Rev.*, **2021**, *121*, 1232.
2. a) E. R. Cooper, C. D. Andrews, P. S. Wheatley, P. B. Webb, P. Wormald, R. E. Morris, *Nature*, **2014**, *430*, 1012.  
 b) R. A. Maia, B. Louis, S. A. Baudron, *CrystEngComm*, **2021**, *23*, 5016.
3. R. A. Maia, B. Louis, S. A. Baudron, *Dalton Trans.*, **2021**, *50*, 4145.
4. M. Teixeira, R. A. Maia, S. Shanmugam, B. Louis, S. A. Baudron, *Micropor. Mesopor. Mat.*, **2022**, *343*, 112148.
5. M. Teixeira, R. A. Maia, L. Karmazin, *CrystEngComm*, **2022**, *24*, 601.
6. R. A. Maia, A. Fluck, C. Maxim, B. Louis, S. A. Baudron, *Green Chem.*, **2023**, *25*, 9103.



## 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

## Modeling gas adsorption in zeolites, taking into account different adsorption mechanisms

C. Miqueu

Université de Pau et des pays de l'Adour, E2S UPPA, CNRS, LFCR, Anglet, France

Gas adsorption in zeolites can be governed by a succession of different mechanisms depending on both the gas and the zeolite, such as adsorption on different cations or cavity filling. In this talk, a methodology based on models that are representative of these adsorption mechanisms is presented for the adsorption of pure gases and their mixtures on different zeolites. As representative examples, the adsorption of carbon dioxide, nitrogen and methane was measured on FAU-13X, LTA-5A and ZSM5 over a very wide range of pressures (from  $10^{-5}$  to 80 bar) and temperatures (from 253 K to 363 K) using a combination of low-pressure, high-resolution manometry and high-pressure gravimetry. These measurements, coupled with those of adsorption enthalpy and adsorption equilibrium of mixtures, as well as microscopic studies available in the literature, have enabled us to establish the link between the structural properties of the zeolites and the adsorption mechanisms of the different gases studied. The macroscopic adsorption models most widely used in the modeling of adsorptive gas separation processes (e.g. Toth, Sips and bi-Langmuir [1]) were then analyzed on the basis of all the experimental data and adsorption mechanisms identified. It was shown that these models do not provide a consistent representation of the various isotherms and heats of adsorption involved [2]. A novel methodology that goes beyond conventional modeling approaches has therefore been proposed. It enables to predict the selectivity of gas mixtures from two adsorption isotherms measured for pure gases within the limits of the temperature range of interest and IAS theory [3].

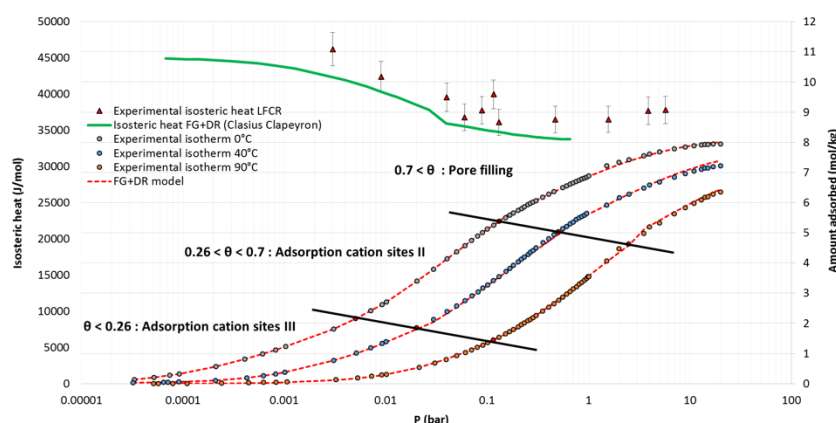


Fig. 1. CO<sub>2</sub> adsorption on FAU-13X

### Références

- [1] Do, D. D. (1998). *Adsorption analysis: equilibria and kinetics* (Vol. 2, pp. 1-18). London: Imperial college press.
- [2] Orsikowsky-Sanchez, A., Plantier, F., & Miqueu, C. (2020). Coupled gravimetric, manometric and calorimetric study of CO<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> adsorption on zeolites for the assessment of classical equilibrium models. *Adsorption*, 26(7), 1137-1152.
- [3] Myers, A. L., & Prausnitz, J. M. (1965). Thermodynamics of mixed-gas adsorption. *AIChE Journal*, 11(1), 121-127.

# KEYNOTES



**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

**Espèces radicalaires dans les zéolithes**

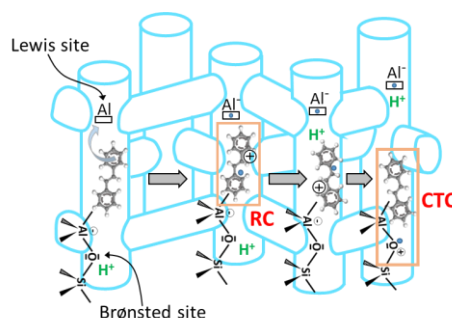
**I. Batonneau-Gener,<sup>a</sup>**

<sup>a</sup> Université de Poitiers, IC2MP

Les zéolithes sont bien connues pour leurs propriétés catalytiques, d'échange ou en tant qu'adsorbants. Ce sont d'ailleurs ces propriétés qui en font des matériaux extrêmement intéressants d'un point de vue industriel. Néanmoins, elles possèdent également la capacité de stabiliser des espèces radicalaires formées à l'intérieur des micropores.<sup>1</sup> Les durées de vie observées pour ces radicaux sont très souvent bien supérieures à celles obtenues en milieu homogène. L'ionisation de la molécule qui engendre cet état de charges séparées peut être initiée soit spontanément soit par photolyse, radiolyse, voie électrochimique ou thermique. Par exemple, il est aujourd'hui bien établi que l'adsorption dans le volume poreux d'une zéolithe d'une molécule aromatique ayant un potentiel d'ionisation relativement bas peut conduire à son ionisation spontanée et à la création d'états de charges séparées très stables. L'effet de confinement est bien souvent une des raisons évoquée pour expliquer cette surprenante stabilité.<sup>2</sup> Néanmoins, les acidités de Bronsted et de Lewis ainsi que la distribution et la force des sites sont également paramètres importants.<sup>3</sup>

La possibilité d'existence de ces espèces a conduit les chercheurs à les intégrer dans leur réflexion. Par exemple, la mise en évidence de radicaux organiques lors de processus catalytiques tels que le MTO, le ETH ou l'oxydation de COV sur zéolithes a bouleversé les schémas réactionnels classiques en établissant leur rôle dans le processus catalytique.<sup>4</sup> Plus récemment, une forte implication de ces espèces radicalaires a été démontrée lors de la synthèse de ZTC (Zeolite Templated Carbon).<sup>5</sup>

Le contrôle des populations de radicaux par l'ajustement des propriétés physico-chimiques des zéolithes devient alors un point clé pour améliorer les performances catalytiques de ces matériaux ou pour l'élaboration de nouveaux matériaux hybrides.



**Fig. 1.** Stabilisation du t-stilbène dans une zéolithe ZSM-5

**Références**

[1] H. Garcia, H. D. Roth, Chem. Rev. 102 (2002) 3947.  
 [2] M. Hureau, A. Moissette, A. Legrand, F. Luche, M. Sliwa, C. Bremard, J. Phys. Chem. C 116 (2012) 9092.  
 [3] T. Crémoux, Batonneau-Gener, A. Moissette, J.-L. Paillaud, M. Hureau, E. Ligner, C. Morais, S. Laforge, C. Marichal, H. Nouali, Phys. Chem.Chem. Phys. 21 (2019) 14892.  
 [4] L. Pinard, K. Ben Tayeb, S. Hamieh, H. Vezin, C. Canaff, S. Maury, O. Delpoux, Y. Pouilloux, Catal. Today 218-219 (2013)57.  
 [5] T. Aumond, I. Batonneau-Gener, Y. Pouilloux, L. Pinard, D. Wissler, M. Moreau, H. Vezin, A. Moissette, A. Sachse, Mater. Today Chem. 26 (2022) 101053.

**ORAUX**



## 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

## Facile synthesis of Zr-MOF/polyester composites for the degradation of nerve agents

Pauline Hardy<sup>a</sup>, Mohamed Taieb Bakouche<sup>a</sup>, Manuela Ferreira<sup>b</sup>, Christine Campagne<sup>b</sup>, Thierry Loiseau<sup>a</sup>, Frédérique Pourpoint<sup>a</sup>, Jeremy Dhainaut<sup>a</sup> and Christophe Volkringer<sup>a</sup>

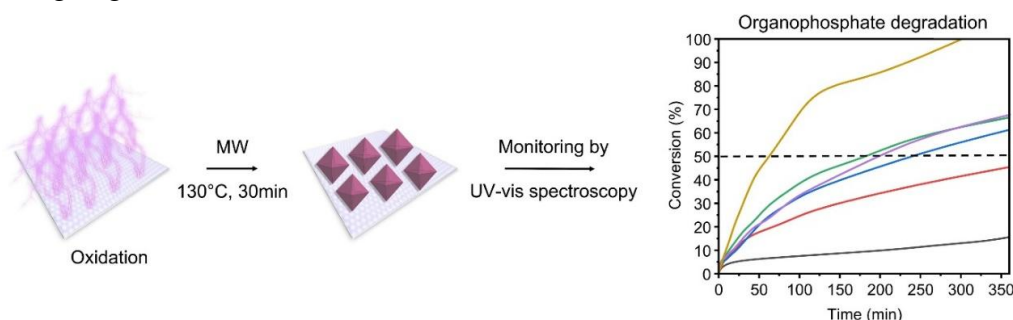
<sup>a</sup> UMR CNRS 8181, Unité de Catalyse et Chimie du Solide, Centrale Lille, CNRS, Univ.Lille, 59800 Lille, France

<sup>b</sup> Univ. Lille, GEMTEX – Laboratoire de génie Matériaux Textiles, 59800 Lille, France

**Keywords:** polyester, nerve agents, degradation, zirconium, composite

Organophosphates belong to the family of neurotoxic agents that are dangerous to humans, since they affect the way nerves transmit signals to muscles. Nowadays, the most famous organophosphate-based chemical warfare agents (CWAs) are Sarin (GB), Soman (GD), or Tabun (GA).<sup>[1]</sup> Zr-based MOFs associated to textile fibers lead to very efficient composites for the capture and the decomposition of CWAs.<sup>[2]</sup> Among the large choice of textiles, polyester fabrics are particularly interesting thanks to their light weight, elasticity, low moisture absorption and resistance. Unfortunately, this high stability and chemical inertness makes them unsuitable for the grafting of nanomaterials on their surface.

In this work, polyester zirconium-based MOF composites were easily synthesized using a two-steps synthesis approach. First, polyester fabric was activated by an oxidation process in order to generate reactive groups at the surface of the fiber. Then, the pre-functionalized fabric is used as a support for the synthesis of nanosized Zr-MOF by microwave synthesis. The resulting composite exhibits very high efficiency for the degradation of organophosphorus nerve agents. Furthermore, the excellent resistance of the different MOF-based composites was confirmed by normed abrasion and artificial ageing tests.<sup>[3]</sup>



**Fig. 1.** Scheme of the strategy used in this study for the fabrication of Zr/Polyester-based composites for the degradation of organophosphate.

## Références

- [1]. Y. Liu, A. J. Howarth, N. A. Vermeulen, S.-Y. Moon, J. T. Hupp, O. K. Farha, *Coordination Chemistry Reviews*, 346, 101–111.
- [2]. N. Couzon, J. Dhainaut, C. Campagne, S. Royer, T. Loiseau, C. Volkringer, *Coordination Chemistry Reviews*, 467, 214598.
- [3]. P. Hardy, M.T. Bakouche, M. Ferreira, C. Campagne, T. Loiseau, F. Pourpoint, J. Dhainaut, C. Volkringer, *submitted*



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

**THEME**

Thème 2 : Applications pour environnement, énergie et santé

Thème 3 : Modélisation et caractérisation de matériaux poreux

**The impact of templates on the local order and properties of aluminophosphates**

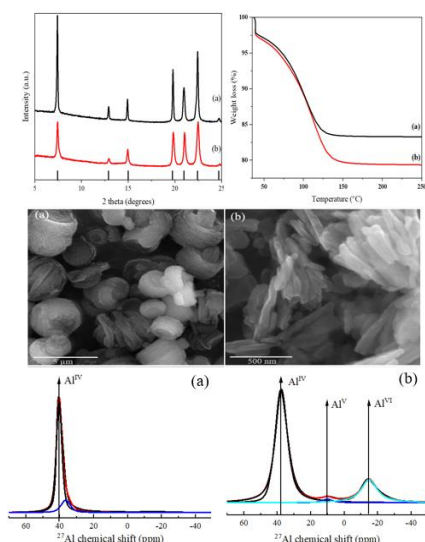
Ludovica Pace,<sup>a</sup> Eddy Dib,<sup>b</sup> Svetlana Mintova<sup>a</sup>

<sup>a</sup> *Laboratoire Catalyse et Spectrochimie (LCS), Normandie University, ENSICAEN, UNICAEN, CNRS, 14000, Caen, France*

<sup>b</sup> *CNRS CEMHTI - UPR3079 CNRS, 45071, Orléans, France*

Aluminophosphates (AIPOs) have been obtained with a wide variety of organic molecules used as templates, however, their exact role is far from being elucidated<sup>1</sup>. While these molecules are known to be structure-directing agents (SDAs) ensuring the charge compensation of heteroatoms, the diversity of the strong and/or weak electrostatic interactions with the framework renders hard the understanding of the atomic organization of AIPOs and thus, the control of their final properties. Then, understanding the role of templates is crucial for a rational design of porous frameworks targeting specific properties<sup>2</sup>.

In this work, we show the impact of the organic templates on the atomic ordering of AIPO- and SAPO-5 synthesized in microwave conditions<sup>3</sup> using a wide panel of analytical methods including X-ray diffraction (XRD), scanning electron microscopy (SEM), inductively coupled plasma (ICP) analysis, thermogravimetric analysis (TGA), nuclear magnetic resonance (NMR) spectroscopy, and Fourier-transform infrared (FT-IR) spectroscopy. The hydrophilic properties of the calcined materials are highly dependent on the selection of templates during the synthesis consequently. This result provides a promising approach to tailor the properties of aluminophosphates-based water adsorbents.



**Fig. 1.** XRD patterns (top left), hydrophilicity profiles (top right), SEM images (middle) and <sup>27</sup>Al NMR spectra (bottom) of AIPO-5 synthesized with two different templates.

**Références**

- [1] L. Gómez-Hortigüela, F. Corà, C. R. A. Catlow, J. Pérez-Pariente, *J Am Chem Soc*, 2004, 12097–12102.
- [2] L. Ye, F. Cao, W. Ying, D. Fang, Q. Sun, *Journal of Porous Materials*, 2011, **18**, 225–232.
- [3] E.P. Ng, D. Tat-Lun Ng, H. Awala, K. L. Wong, S. Mintova, *Mater Lett*, 2014, **132**, 126–129.





**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

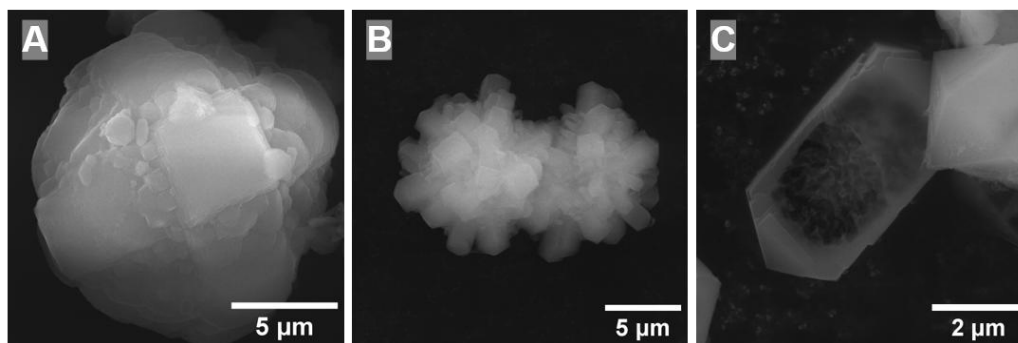
**Morphology control of ZSM-11 zeolite using novel templates and additives**

**Junwei Wu,<sup>a</sup> Qiudi Yue,<sup>a</sup> Svetlana Mintova<sup>a,\*</sup>**

<sup>a</sup> *Laboratoire Catalyse et Spectrochimie (LCS), CNRS, 14050 Caen, France.*

ZSM-11 with MEL framework structure is a promising zeolite for applications in catalysis, owing to its rapid intra-crystalline diffusion due to presence of only straight channels [1]. To promote the crystallization of ZSM-11, tetrabutylammonium (TBA) cation is commonly used as an organic template. However, an intergrowth of ZSM-11/ZSM-5 phases is often presented due to the similarity of the two phases, making the synthesis of pure-phase ZSM-11 challenging. Therefore, the discovery of alternative templates for preparation of pure ZSM-11 zeolite with variable morphology is of great interest. Recently, 2,2-diethoxyethyl-trimethylammonium (DEOTA), N,N-diethyl-3,5-dimethylpiperidinium (DEDMP), and 1,8-diaminooctane (DAO) have been identified as organic templates that possibly facilitate the synthesis of ZSM-11. The former two templates are not commercially available, on the other hand, DAO usually generates micron-sized crystals provoking slow diffusion.

In this work, DAO was employed as the organic template to prepare ZSM-11 zeolite, and the synthetic parameters, i.e. the H<sub>2</sub>O/SiO<sub>2</sub> and DAO/SiO<sub>2</sub> ratios were optimized. To decrease the diffusion pathway in the zeolite crystals, two strategies were explored: (1) generation of nanosized crystallites forming aggregates and (2) formation of hollow crystals. It was found that flower-like ZSM-11 crystals can be synthesized using an additive. In addition, hollow crystals were obtained by altering the order of addition of the reagents in the reaction mixture, following the dissolution-recrystallization mechanism.



**Fig. 1.** SEM images of ZSM-11 zeolite crystals synthesized using DAO as SDA (A) synthesis, an additive (B), and altering the order of mixing of reagents (C).

**Références**

1. Shen, Y., et al., *Optimized Synthesis of ZSM-11 Catalysts using 1,8-Diaminooctane as a Structure-Directing Agent*. *Chemphyschem*, 2018. **19**(4): p. 529-537.



THÈME

- 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

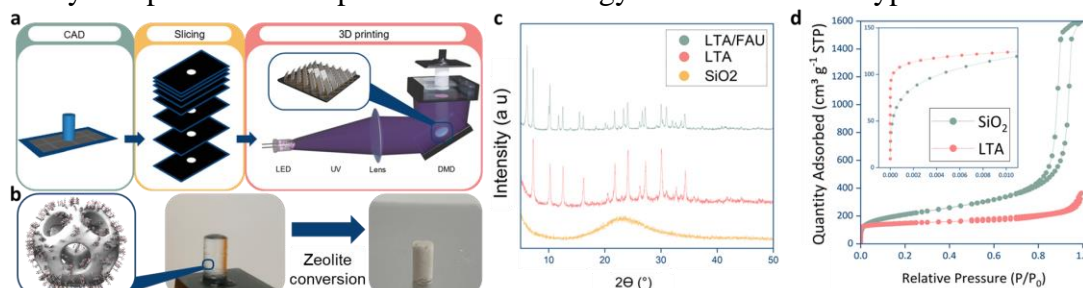
**Manufacturing of zeolite monoliths through pseudomorphic transformation of 3D printed mesoporous silica monolith**

T. Gaillard<sup>a</sup>, T. Aubert<sup>a</sup>, A. Galarneau<sup>a</sup>

<sup>a</sup> ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France

In the past few years, 3D printing has gained a lot of interest in material chemistry, giving access to highly complex structures that could not be produced using conventional approaches. Among 3D printing techniques, digital light processing (DLP) allows for the rapid printing of monolithic structures with high freedom of design and high accuracy until a 10  $\mu\text{m}$  resolution (**Fig. 1a**). Printed structures can be tailored to address specific needs, for instance through the implementation of complex and well controlled macropore networks. In parallel, zeolites have outstanding specific properties for many applications (catalysis, adsorption) due to their controlled microporosity. The combination of 3D printing with zeolites would hence generate important opportunities for the manufacturing of hierarchically porous zeolites monoliths for process intensification.

Here, we introduce a novel pathway for the fabrication of 3D zeolite monoliths through the pseudomorphic transformation of DLP printed mesoporous silica structures. These monoliths are first printed from inks made of mesoporous silica nanocages functionalized with photosensitive ligands<sup>[1]</sup>. In contrast to common nanocomposite approaches, these inks do not require any resin or binder. The resulting silica monoliths have very low organic fractions and can be directly converted into zeolites without any calcination step (**Fig. 1b**). The 3D silica monoliths are then converted into 3D LTA or LTA/FAU-X monoliths (**Fig. 1c,d**) by pseudomorphic transformation<sup>[2,3]</sup>. In future, this process could be extended to a large variety complex 3D macroporous structures as gyroids and to other type of zeolites.



**Fig. 1.** (a) Illustration of the DLP printing workflow. (b) Pictures of a 3D printed mesoporous monolith based on silica cages, before and after its conversion into zeolite. XRD patterns (c) and nitrogen sorption isotherms at 77K (d) of 3D silica and LTA, LTA/FAU-X monoliths.

**References**

- [1] T. Aubert, J. Huang, K. Ma, T. Hanrath, U. Wiesner, Porous cage-derived nanomaterial inks for direct and internal three-dimensional printing, *Nature Communications*, 11 (2020) 4695.  
 [2] B. Said, T. Cacciaguerra, F. Tancret, F. Fajula, A. Galarneau, Size control of self-supported LTA zeolite nanoparticles monoliths, *Microporous and Mesoporous Materials*, 227 (2016) 176.  
 [3] Y. Didi, B. Said, et al., Synthesis of binderless FAU-X (13X) monoliths with hierarchical porosity, *Microporous and Mesoporous Materials*, 281 (2019) 57



**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

**Synthèse de Chabazite cœur-couche possédant une surface hautement silicique**

Clément Got<sup>a,b</sup>, Alain Tuel<sup>b</sup>, Bogdan Harbuzaru<sup>a</sup>

<sup>a</sup>IFP Energies Nouvelles, Direction Catalyse et Séparation, 69360 Solaize, France

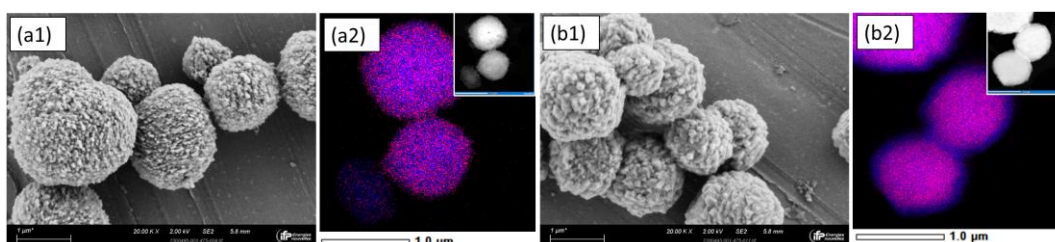
<sup>b</sup>IrceLyon, CNRS, 69626 Villeurbanne, France

De nombreuses zéolithes sont connues pour perdre leur activité catalytique en présence d'eau dû à la forte interaction avec leurs sites actifs. Dans cette étude, une zéolite cœur-couche de type chabazite (CHA) a été synthétisée pour la première fois en milieu basique avec une grande différence de ratio Si/Al entre le cœur et la couche pour lui conférer des propriétés hydrophobes<sup>1,2</sup>.

Le cœur est synthétisé d'après une méthode précédemment décrite dans la littérature<sup>3</sup>. Sans calcination, le cœur est plongé dans un gel hautement silicique (LUDOX-HS40, TMAOH, NaOH, H<sub>2</sub>O) avant traitement hydrothermal. Le cœur-couche formé est purifié et calciné.

L'analyse DRX montre que le matériau de cœur et le cœur-couche possèdent une structure de type CHA sans impuretés. Le ratio Si/Al mesuré par fluorescence X augmente indiquant qu'une zéolite plus silicique a été formée. D'après les images MEB, le cœur-couche est formé d'agrégats sphériques plus gros que le cœur (augmentation de 10-15%) avec une morphologie de surface différente suggérant le dépôt d'une couche uniforme (Fig 1-b1). Une cartographie STEM-EDS permet de confirmer la présence d'une couche hautement silicique d'environ 150nm d'épaisseur en accord avec la croissance de taille des particules (Fig 1-b2).

Ces matériaux seront échangés au Cu et employés pour la réduction catalytique sélective par l'ammoniaque des NO<sub>x</sub> présents dans les fumées d'échappements (moteurs thermiques et/ou hydrogène). L'influence de la couche silicique sur l'activité et la stabilité hydrothermale de la zéolite en présence d'eau sera évaluée.



**Fig. 1.** Images MEB et STEM-EDS du cœur (a1,a2) et du cœur-couche (b1,b2) (Si : bleu, Al : rose)

**Références**

1. W. Wu (Pacific Industrial Development Corporation), US20190336954A1, 2019
2. M. Miyamoto, *Chemical Engineering Journal*, 2019, 363, 292-299
3. Y. Guo, *Chem. Asian J.* 2018, 13, 3222-3230

**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

**Is there any benefit of using the gallate complexing group to prepare new MOFs: the key impact of residual phenolic protons**

N. Gedikoglu,<sup>a</sup> M. Paris,<sup>a</sup> N. Guillou,<sup>b</sup> C. Martineau,<sup>b</sup> G. Mouchaham,<sup>b</sup> N. Heymans,<sup>c</sup> G de Weireld,<sup>c</sup> A. Fateeva,<sup>d</sup> E. Bloch,<sup>e</sup> S. Bourrelly,<sup>e</sup> J. Ostolaza-Paraiso,<sup>f</sup> D. Fairen-Jimenez,<sup>f</sup> **T. Devic<sup>a</sup>**

<sup>a</sup> *IMN, CNRS - Nantes Université, Nantes, France*

<sup>b</sup> *ILV, CNRS - Université Paris-Saclay, Versailles, France*

<sup>c</sup> *Faculté Polytechnique, Université de Mons, Mons, Belgium*

<sup>d</sup> *LMI, CNRS – Université Lyon 2, Villeurbanne, France*

<sup>e</sup> *MADIREL, CNRS – Université Aix-Marseille, Marseille, France*

<sup>f</sup> *6A2ML, University of Cambridge, United Kingdom*

In the field of MOFs, phenolate complexing groups were found in the last decade to be valuable alternatives to more conventional carboxylates and azolates, notably because of their non-innocent character, which is at the origin of the unique electronic conductivity, redox activity or magnetic properties of the derived MOFs. While catecholate (1,2-dioxobenzene) ligands have been initially considered, we and others found a valuable interest in the use of the gallate (1,2,3-trioxobenzene) unit.

First, thanks to its high charge and high pKa, such a complexing group allows achieving the synthesis of MOFs rather easily in the presence of water, even in some cases at very basic pH.<sup>1</sup> The thorough investigation of the synthetic conditions in the last years allowed the identification of well defined, robust enough, inorganic building units (IBUs), notably with high charge cations (Zr(IV)<sup>2</sup>). Such IBUs were further exploited for the design of new MOFs. Various characterization tools (IR, solid state NMR,...) showed that, compared to the more conventional complexing groups, the gallate motif typically binds to cations while remaining partially protonated.<sup>1,2,4</sup> Through selected examples, we will here show how this unique feature affects the properties of the derived solids. The following items will be discussed:

- the compositional diversity: the amount of remaining protons and charge of the framework cations are correlated. This allows preparing isostructural MOFs based on cations of various charges (*e.g.* La(III) and Zr(IV)).<sup>2</sup>
- the chemical stability especially towards water or competitive complexing species such as phosphates is also strongly affected by the amount of residual protons.<sup>1,2,4</sup>
- the sorption properties: these protons are highly acidic, and can thus act as strong adsorption sites, notably for greenhouse gases such as CO<sub>2</sub>.<sup>3,4</sup>

**Références**

- [1] T. Hidalgo et al., *J. Mater. Chem. B* **2017**, 5, 2813; L. Cooper et al., *Chem. Commun.* **2015**, 51, 5848.  
[2] G. Mouchaham et al., *Chem. Commun.* **2017**, 53, 7661; G. Mouchaham et al., *Angew. Chem. Int. Ed.* **2015**, 54, 13297.  
[3] N. Heymans et al., *J. Phys. Chem C.* **2020**, 124, 3188.  
[4] N. Gedikoglu et al., *submitted*.


**THEME**

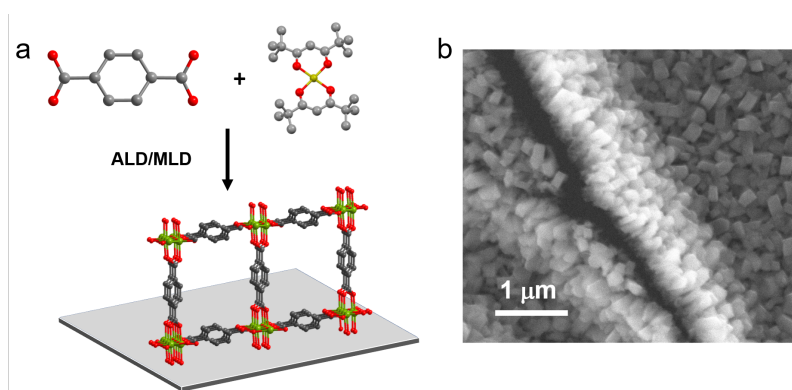
- Thème 1 : Elaboration et mise en forme de matériaux poreux  
 Thème 2 : Applications pour environnement, énergie et santé  
 Thème 3 : Modélisation et caractérisation de matériaux poreux

**MOF thin films growth by Atomic/Molecular Layer Deposition**

B. Gikonyo, F. Liu, S. De, C. Journet, C. Marichy, A. Fateeva

*Laboratoire des Multimatériaux et Interfaces, Université Lyon, Université Claude Bernard Lyon 1, UMR CNRS 5615, F-69622 Villeurbanne, France, email: [alexandra.fateeva@univ-lyon1.fr](mailto:alexandra.fateeva@univ-lyon1.fr)*

Atomic/Molecular Layer Deposition (ALD or MLD) techniques are based on sequential self-limiting successive reactions, usually applied for the deposition of conformal and homogeneous thin films.<sup>1</sup> More recently an implementation of this technique to porous structures including Metal Organic Frameworks (MOFs) started to arouse interest for several reasons.<sup>2</sup> Indeed, ALD is a vapour/solid interfacial process that avoids the use of toxic solvents as well as time consuming work up steps and activation procedures. In ALD, the use of reactive organometallic precursors promotes fast and efficient chemical reactions. In our group, we are exploring ALD approach towards both (i) the post-synthesis modification of stable MOFs<sup>3</sup> and (ii) the direct MOF thin films synthesis by ALD.<sup>4</sup> The later topic is most challenging. Indeed, although a few MOFs have been grown by ALD recently, obtaining layers with good crystallinity and porosity remains arduous.<sup>5–7</sup> We investigated the direct growth of copper-based MOFs by ALD, and demonstrate that a crystalline MOF phase could be directly obtained on different kinds of substrates, evidencing an oriented growth process (Figure 1).



**Fig. 1.** Representation of the ALD/MLD growth of MOF thin films of copper terephthalate (a), scanning electron microscopy image of a thin film formed of MOF crystallites (b).

**References**

- George, S. M. Atomic Layer Deposition: An Overview. *Chemical Reviews* **110**, 111–131 (2010).
- Su, P., Tu, M., Ameloot, R. & Li, W. Vapor-Phase Processing of Metal–Organic Frameworks. *Acc. Chem. Res.* **55**, 186–196 (2022).
- De, S. *et al.* Vapor-Phase Infiltration inside a Microporous Porphyrinic Metal–Organic Framework for Postsynthesis Modification. *Inorg. Chem.* **59**, 10129–10137 (2020).
- Gikonyo, B. *et al.* Investigating the vapour phase synthesis of copper terephthalate metal organic framework thin films by atomic/molecular layer deposition. *Dalton Trans.* **52**, 211–217 (2023).
- Ahvenniemi, E. & Karppinen, M. Atomic/molecular layer deposition: a direct gas-phase route to crystalline metal–organic framework thin films. *Chem. Commun.* **52**, 1139–1142 (2016).
- Ahvenniemi, E. & Karppinen, M. In Situ Atomic/Molecular Layer-by-Layer Deposition of Inorganic–Organic Coordination Network Thin Films from Gaseous Precursors. *Chem. Mater.* **28**, 6260–6265 (2016).
- Lausund, K. B. & Nilsen, O. All-gas-phase synthesis of UiO-66 through modulated atomic layer deposition. *Nature Communications* **7**, 13578 (2016).

**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

**Microporous materials for energy-saving atmospheric water harvest**

**H. Zhao,<sup>a, b</sup>** X. Yang,<sup>b</sup> R. Guillet-Nicolas,<sup>a</sup> V. Yasnou,<sup>a</sup> V. Valtchev,<sup>a,\*</sup>

<sup>a</sup> *Laboratoire Catalyse et Spectrochimie, Normandie University, ENSICAEN, UNICAEN, CNRS, F-14050 Caen, France.*

<sup>b</sup> *The ZeoMat Group, Qingdao Institute of Bioenergy and Bioprocess Technologies, CAS, Laoshan District, CN-266101 Qingdao, China.*

Freshwater scarcity is a growing global challenge that has become the sixth most urgent issue among the current global “poly-crises”. Atmospheric water is emerging as an alternative resource, and the related adsorption-based atmospheric water harvesting (AWH) has been proposed as a promising strategy. Ideal sorbent materials for AWH are required to have high water capacity, fast water adsorption/desorption kinetic, low energy consumption for regeneration, stable cycling performance, and reasonable cost.

As one of the important water sorbents, zeolites show high hydrophilicity. However, zeolites need a high temperature for full regeneration ( $> 200^{\circ}\text{C}$ ), resulting in high energy consumption. Alternatively, metal-organic frameworks (MOF) are proposed as a class of adsorbents with energy-efficient regeneration, while the poor long-term hydrothermal stability, and challenges on cost and toxicity hinder their practical applications seriously.

Aluminophosphates (AIPOs) are zeolitic materials exhibiting a neutral framework. They generally show water adsorption isotherms with an S-shape and a high water capacity similar to zeolites. More importantly, AIPOs show a much easier water desorption process at low temperature ( $< 90^{\circ}\text{C}$ ), similar to MOFs. Their consequent lower energy request makes the energy-saving and facile AWH technology achievable.

In this work, we systematically assess 12 selected microporous materials out of zeolites, AIPOs, and MOFs. Through a comparative study of water adsorption isotherms, desorption energies, kinetics, and other relevant parameters at the same conditions, the zeotype aluminophosphate with AEI framework topology (AIPO-18) stands out. AIPO-18 shows a high potential to extract water in arid regions. It shows 0.29 g/g water uptake in a very narrow range of low relative humidity (10%-13%) and is almost completely regenerated below  $70^{\circ}\text{C}$ . These conditional parameters are favored for facile designs of energy-saving cycling processes. Moreover, AIPO-18 shows a negligible decrease in capacity over 10 cycles of adsorption and desorption tests at very harsh conditions. Therefore, we propose AIPO-18 as a potential candidate for developing energy-saving atmospheric water harvest (AWH) technology to extract fresh water from “dry” air.

Detailed information and an in-depth discussion will be presented on the 12 studied sorbents.

**References:**

- [1] X. Zhou, H. Lu, F. Zhao, G. Yu, *ACS Materials Lett.* 2, 671 – 684 (2020).  
[2] E.-P. Ng, S. Mintova, *Microporous and Mesoporous Materials.* 114, 1–26 (2008).

**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

**Positive effects of controlled nanoconfined metals for LOHC regeneration****M. El Zayed<sup>a</sup>, P. Bazin<sup>a</sup>, F. Dalena<sup>a</sup>, R. Zhang<sup>a</sup> and L. Pinard<sup>a</sup>**<sup>a</sup> *Laboratoire de Catalyse et Spectrochimie (LCS), Université de Caen, CNRS, F-14000, Caen, France*

Hydrogen is becoming an essential vector of the global energy mix as we move towards renewable energy and decarbonization. However, the transportation and storage of Hydrogen pose logistical and safety challenges. Liquid Organic Hydrogen Carriers (LOHC) offer a compelling solution for establishing a cleaner and more sustainable Hydrogen supply chain [1].

The family of carrier selected is Toluene (“TL”) and MethylCycloHexane (“MCH”). These carriers are preferred due to their low toxicity, chemical stability, and ease of handling and storage. They can be stored in existing oil infrastructures at ambient conditions without losses during transport or storage, offering significant advantages over other options. The concept is binding H<sub>2</sub> to TL. This step is called hydrogenation and is performed at the location where H<sub>2</sub> is produced. Then liquid MCH is easily and safely stored and transported to importing regions. At this location, chemical binding is broken to release H<sub>2</sub> and TL. This step is called dehydrogenation. TL is then returned to the producing country to complete the cycle (regeneration). Recently, Axens joined forces with Chiyoda Corporation in 2022 to offer the complete LOHC chain. Each company offers TL hydrogenation and SPERA MCH DeHydrogenation respectively.

The aim of this study is to develop a hydrogenation catalyst for the regeneration of toluene. Traditional catalysts for hydrogenation under mild conditions (low temperature and atmospheric pressure) are based on well dispersed clusters of noble metals (Pt, Pd and Rh) on supports of alumina, silica and carbon. However, the hydrogenation activity is boosted when the metal nanoparticles are dispersed on a microporous material such as zeolite [2,3]. Gounder [4] and Bhan [5] have associated the enhanced activity of acid zeolites for the hydrogenation of unsaturated hydrocarbons with the ability of the Brønsted acid sites of zeolites to stabilize the reaction intermediates. The role of Brønsted acid as a possible driving force for increasing the hydrogenation activity (A<sub>H</sub>) of the Pt site remains an open question. The confinement of the nanometer-sized metal particle could also play an important role in increasing the A<sub>H</sub>. To confirm this, it will be important to compare it with another acid-free microporous material, such as 3D carbon structures (Zeolite Templated Carbons).

**Acknowledgement:** The Authors thanks the Region Normandie for funding the BioDNH “Chaire d’excellence”.

**References**

- [1] E. Southall and L. Lukashuk, Johnson Matthey Technol., 6 (2022) 271–284.
- [2] J. Chupin, N.S. Gnep, S. Lacombe, M. Guisnet, Appl. Catal. Gen., 206 (2001) 43-56.
- [3] N. Batalha, J. D. Comparot, A. Le Valant, Catal. Sc. Tech, 12 (2022) 12, 1117.
- [4] R. Gounder and E. Iglesia, J. Catal., 277 (2011) 36–45.
- [5] S. S. Arora and A. Bhan, J. Catal., 383 (2020), 24–32



## 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

## Films composites antibactériens à base de MOF ZIF-8/ZIF-dia(Zn)

L. Premet,<sup>a,b</sup> E. Oheix,<sup>a</sup> G. Chaplais,<sup>a</sup> L. Pieuchot,<sup>a</sup> T. J. Daou<sup>b</sup>

<sup>a</sup> Institut de Science des Matériaux de Mulhouse (IS2M), Université de Haute Alsace (UHA), Université de Strasbourg (UniStra), CNRS, IS2M UMR 7361, F-68100 Mulhouse, France

<sup>b</sup>APTAR-CSP Technologies, 67110 Niederbronn-les-Bains

La contamination bactérienne est une problématique industrielle majeure dans les domaines agroalimentaires et pharmaceutiques. Elle peut en effet affecter la qualité d'un produit et mettre en danger la santé de l'utilisateur. Les matériaux de type MOF (Metal-Organic Framework) apparaissent comme d'excellents composés antibactériens grâce à leurs compositions chimiques et/ou leurs capacités à encapsuler des substances agissant comme agents bactéricides [1]. Les MOFs ZIF-8 et ZIF-dia(Zn) constituent des polymorphes formés d'ions divalents de zinc tétracoordinés par des ligands de type imidazolate [2], et sont utilisés dans l'étude menée pour leurs propriétés bactéricides. Cependant, ces matériaux doivent être mis en forme afin d'être utilisés dans un emballage. Plusieurs formulations de composites polymères/MOFs ont été extrudées sous forme de film puis testées sur *Escherichia coli* (*E. coli*) par différentes méthodes de test. Les résultats indiquent une activité antibactérienne par contact, à partir de 32 % en masse de MOF dans le composite (Figure 1). Cette activité antibactérienne au contact sera couplée au relargage contrôlé d'agents antibactériens volatils (composés organiques volatils) stockés dans la microporosité du MOF au sein du film, permettant une action antibactérienne dans l'ensemble de l'emballage.

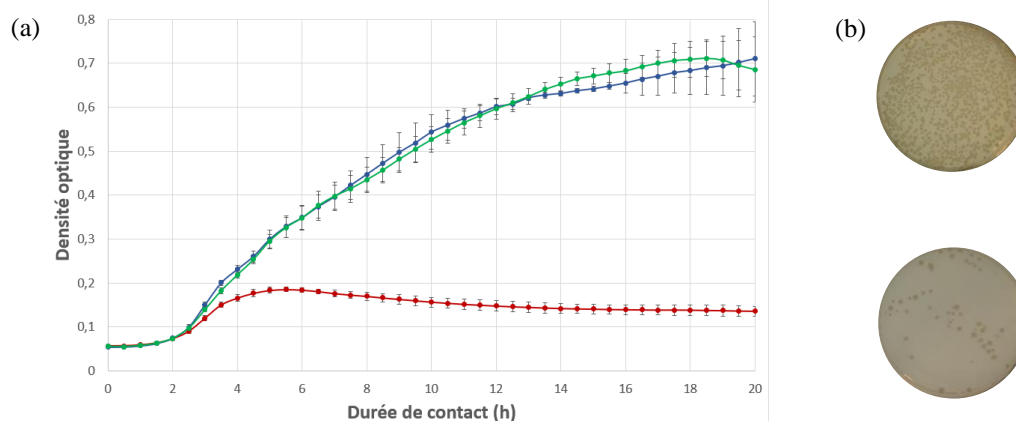


Figure 1: (a) Evolution de la densité optique d'une solution de bactéries *E. coli* à  $10^6$  CFU/mL, en contact avec (-) film blanc; (-) film à 32 % ZIF-8/ZIF-dia(Zn); (-) film à 15 % ZIF-8/ZIF-dia(Zn); (b) Représentation de l'activité antibactérienne sans (en haut) et avec le film à 32 % de ZIF-8/ZIF-dia(Zn) (en bas)

[1] Karimi Alavijeh, R.; Beheshti, S.; Akhbari, K.; Morsali, A., *Polyhedron* **2018**, *156*, 257-278.

[2] Shi, Q.; Chen, Z.; Song, Z.; Li, J.; Dong, J., *Angew. Chem. Int. Ed.* **2011**, *50* (3), 672-675.





**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

**Innovative approaches for recycling old batteries solution through the precipitation of ZIFs**

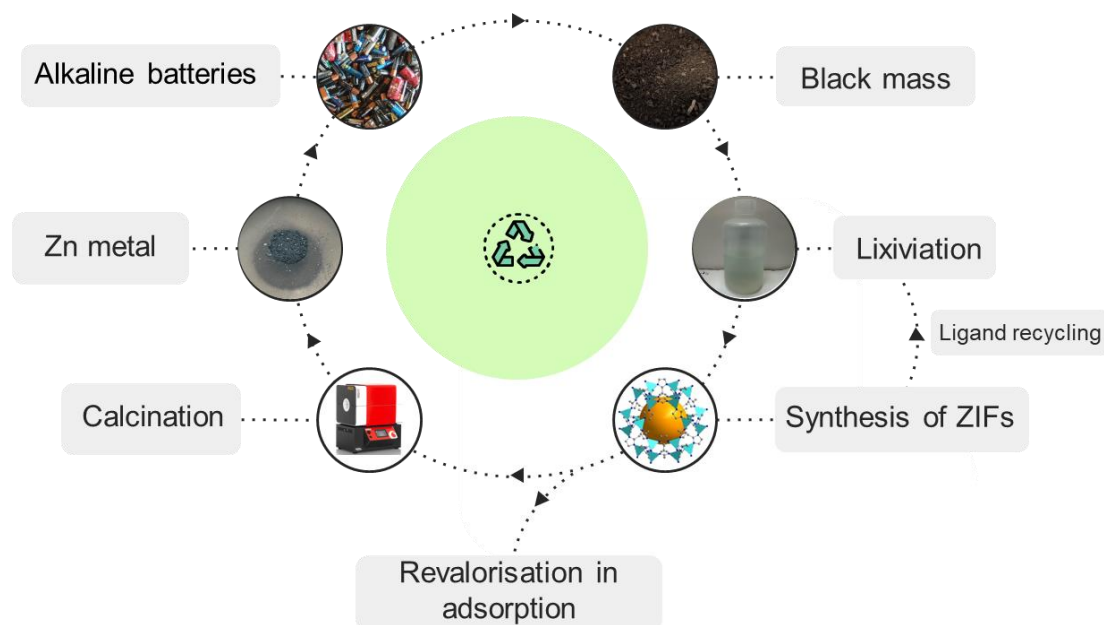
D. Andriotou,<sup>a</sup> G. Frajer,<sup>a</sup> A. Roussey,<sup>a</sup> E. Billy,<sup>a</sup> D. Peralta<sup>a</sup>

<sup>a</sup>Univ. Grenoble Alpes, CEA, LITEN, DEHT, 38000 Grenoble, France

Up to this day, the recycling process in primary batteries involves (hydro) metallurgic processes to produce drip trays, a rather high cost procedure for a low cost material. Herein, we report the selective precipitation of zinc into Zeolitic Imidazolate Frameworks (ZIFs) from a polymetallic aqueous solution, derived from a black mass sample of alkaline (primary) batteries containing metals like Zn, Mn, Ni, Cu, Al, Fe and Co. The synthesis conditions were adapted in order to switch from a methanolic to an aqueous solution, as well as using sulfate precursors instead of nitrates. With the help of benzimidazole or 2-methylimidazole, ZIF-7-III and ZIF-8 precipitated accordingly, leading to a recovery of more than 99 % of zinc in a one-step and one-pot reaction.

Both materials (ZIF-7-III and ZIF-8) were calcined in hydrogenated argon atmosphere, forming metal zinc that was collected as a deposit around the furnace tube and could be involved in the making of new alkaline or Zn-air batteries. The high BET area of ZIF-8 (1300-2000 m<sup>2</sup>/g) permits the further valorization in adsorption and the trapping of propylene and propane.

Finally, more than 50 % of the ligand can be easily recycled and used at new in the process of precipitation. Both loops involve a less energy consuming process, isolating a product of a high value. The closed loop provides a pathway in order to reassemble alkaline batteries, whereas the open loop permits the use in high-importance procedures.



**Fig. 1.** Schematic representation of the main recycling loop with the help of ZIFs.


**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

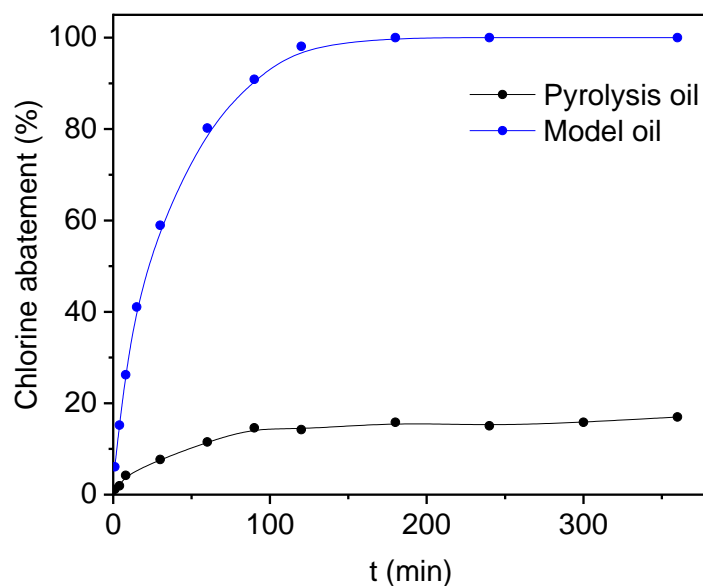
**Purification des huiles de pyrolyse par adsorption sur des zéolithes modifiées**

Léa Mussard<sup>a</sup>, Isabelle Batonneau-Gener<sup>a</sup>, Pierre Moreau<sup>b</sup>

<sup>a</sup> IC2MP, UMR 7285 CNRS, 4 rue Michel Brunet, 86073, Poitiers (France).

<sup>b</sup> Plastic Energy, 65 Carter Lane EC4V 5DY London, UK.

L'obtention d'huiles de pyrolyse issues du recyclage chimique des plastiques, est une alternative au recyclage mécanique permettant la production de polymères recyclés ou de carburants alternatifs. A l'issue du procédé catalytique de pyrolyse, ces huiles contiennent des impuretés à l'état de trace. Afin d'améliorer la qualité finale de l'huile, des éléments tels que le chlore, peuvent être éliminés ex-situ par adsorption. Des études ont démontré une bonne affinité des zéolithes pour l'élimination de molécules organochlorées [1-3]. Dans cette communication, l'impact de la composition chimique d'une zéolithe FAU de type X sur l'abattement en chlore d'une huile modèle sera présenté. Nos travaux ont notamment montré que la basicité des zéolithes n'était pas le seul paramètre à considérer pour augmenter l'abattement en chlore des huiles (figure 1). Leur composition et notamment la teneur en aromatique doivent être considérées dans l'ajustement des propriétés chimiques de l'adsorbant, afin de limiter les adsorptions compétitives indésirables et de maintenir une bonne sélectivité vis-à-vis des organochlorés [4].



**Fig. 1.** Cinétiques d'abattement en chlore après adsorption d'une huile modèle composée de 1-chloroheptane et de n-dodécane et d'une huile de pyrolyse, sur la zéolithe FAU de type X.

Dans ce sens, des échanges ioniques ont été réalisés avec succès pour améliorer la sélectivité des matériaux vis-à-vis du chlore.

**Références**

- [1] : Y. Ou, J. Dy, D. Rosenfeld, U.S. Pat. No. 5,107,061 (1992)  
[2] : R. Ma, J. Zhu, B. Wu, X. Li, *Chem. Eng. Res. Design*, **114**, 321-330 (2016)  
[3] : H. Valdés, A.L. Riquelme, V. A. Solar, F. Azzolina-Jury, F. Thibault-Starzyk, *Separ. Purif. Technol.* **258**, 118080 (2021)  
[4] : C. Jiqun, Z. Xiaojun, Z. Yin, *China Pet. Process. Petrochemical Technol.* **19**, 20-26 (2017)

**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

## Charge Transfer Complexes between Gaseous Iodine and MOF Materials: Exploring Dynamics and Reactivity

Pedro Henrique Morais Andrade<sup>1</sup>, Christophe Volkringer<sup>2</sup>, Thierry Loiseau<sup>2</sup>, Hervé Vezin<sup>1</sup>,  
**Matthieu Hureau<sup>1</sup>**, Alain Moissette<sup>1</sup>

<sup>1</sup> *Laboratoire de Spectroscopie pour les Interactions, la Réactivité et l'Environnement, Université de Lille – Sciences et Technologies, 59655 - Villeneuve d'Ascq, France.*

<sup>2</sup> *Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 - UCCS - Unité de Catalyse et Chimie du Solide, F-59000 Lille, France.*

This study investigates MOFs (UiO-6x, MIL-125, CAU-1) for trapping iodine. Hafnium-based UiO-66 compounds show enhanced iodine uptake compared to zirconium. Crystal size affects adsorption kinetics, and Ti-based MIL-125 MOFs exhibit faster kinetics with stable  $I_3^-$  species. The study also highlights titanium's unique influence on  $I_2$  adsorption, reduction, and desorption mechanisms, emphasizing how porous materials alter properties and stabilization, impacting adsorption and reactivity.

In the study of UiO-66 materials, the alteration of metal ratios (Hf/Zr) yielded intriguing results. UiO-66(Hf) exhibited a smaller lattice parameter, higher crystallite size, and smaller specific surface area compared to its parent UiO-66(Zr). Notably, UiO-66(Hf) demonstrated enhanced iodine capture ( $285 \text{ g.mol}^{-1}$ ) compared to UiO-66(Zr) ( $230 \text{ g.mol}^{-1}$ ) and facilitated the kinetic evolution of  $I_2$  into  $I_3^-$  after 16 hours of filtration.

The investigation extended to UiO-67-NH<sub>2</sub>, where diverse metal contents (Zr, Zr/Hf, and Hf) were explored for iodine capture. The results showed that UiO-67-NH<sub>2</sub>(Hf) outperformed, capturing an impressive  $3428 \text{ g.mol}^{-1}$  of iodine after 48 hours, compared to UiO-67-NH<sub>2</sub>(Zr/Hf) ( $2835 \text{ g.mol}^{-1}$ ) and UiO-67-NH<sub>2</sub>(Zr) ( $1658 \text{ g.mol}^{-1}$ ). Raman spectroscopy confirmed the transformation of  $I_2$  into  $I_3^-$  through the identification of bands related to "perturbed"  $I_2$  and  $I_3^-$  at about 170 and 107  $\text{cm}^{-1}$ , respectively. Spatial distribution analysis revealed distinct concentrations of  $I_2$  and  $I_3^-$  in bimetallic samples, attributed to differences in diffusion processes influenced by crystal size.

The exploration of MIL-125(Ti), MIL-125(Ti)-NH<sub>2</sub>, and CAU-1(Al)-NH<sub>2</sub> highlighted MIL-125(Ti)-NH<sub>2</sub> as a standout performer in iodine uptake. After 72 hours, it trapped  $11.0 \text{ mol.mol}^{-1}$  of  $I_2$ , surpassing MIL-125(Ti) ( $8.7 \text{ mol.mol}^{-1}$ ) and CAU-1(Al)-NH<sub>2</sub> ( $4.2 \text{ mol.mol}^{-1}$ ). The enhanced capability of MIL-125(Ti)-NH<sub>2</sub> was attributed to its amino group, smaller band gap (2.5 eV), and efficient charge separation mechanisms. EPR spectroscopy revealed charge separation in MIL-125(Ti) upon UV light irradiation. In contrast, CAU-1(Al)-NH<sub>2</sub> exhibited a purely linker-based transition, influencing the recombination of photogenerated charge carriers. Raman spectroscopy tracked the conversion of gaseous  $I_2$  into  $I_n^-$  and then  $I_3^-$ , emphasizing the importance of effective charge separation and smaller band gaps in increasing iodine uptake capacity.

Finally, using  $I_2@MIL-125$  and  $I_2@MIL-125-NH_2$ , the stability of  $I_2$  and  $I_3^-$  were evaluated using TGA and *in-situ* Raman spectroscopy. Both MOFs exhibited stability up to 300 °C and similar specific surface area values. Desorption experiments highlighted the role of -NH<sub>2</sub> groups in stabilizing  $I_3^-$  species. The Albery model was applied to assess desorption kinetics, showing longer lifetimes for iodine species in  $I_2@MIL-125-NH_2$ , attributed to a rate-limiting step involving the interaction between anionic iodine species and organic cation radicals.



## 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

### How does a bottom-up approach using biomass for the synthesis of hierarchical ZSM-5 zeolites affect the MTO reaction?

C. Longue<sup>a,b</sup>, Y. Zhang<sup>a</sup>, Q. Zheng<sup>a</sup>, R. Bingre<sup>a</sup>, C.G. Flores<sup>a</sup>, A.V. Silva<sup>c</sup>, M.M. Pereira<sup>c</sup>, L. Pinard<sup>b</sup>, B. Louis<sup>a</sup>

<sup>a</sup> Institute of Chemistry and Processes for Energy, Environment and Health, ICPEES, UMR 7515, CNRS-University of Strasbourg, 25, rue Becquerel, F-67087 Strasbourg Cedex 02, France

<sup>b</sup> ENSICAEN - Laboratoire Catalyse & Spectrochimie – LCS 6, Boulevard Maréchal Juin, F-14050 Caen Cedex 4, France

<sup>c</sup> LACES, Universidade Federal do Rio de Janeiro, Centro de Tecnologia, Avenida Athos da Silveira Ramos, 149, Ilha do Fundão, Rio de Janeiro, RJ, 21941-909, Brazil

Chemistry relies on the design and control of systems over multiple-length scales ranging from the molecule to the crystal [1]. The assembly at the molecular level involves at least two species, based on non-covalent interactions (hydrogen bonding, electrostatic forces, van der Waals forces, metal-ion coordination), being the cornerstone of long-range organization [2]. Though covalent bonding prevails in inorganic porous solids, the latter materials are often meta-stable, being produced after successive meta-stable steps [3]. For instance, crystalline microporous aluminosilicates are typically produced (under hydrothermal conditions) via a sol-gel process using: a silicon and an aluminum-source, a mineralising agent and an organic structure directing agent (OSDA). These ingredients are allowed to dissolve in water, being then placed under autogenous pressure at temperatures higher than 100°C. The formation of the zeolite crystalline structures is governed by electrostatic, van der Waals and hydrophobic forces known as supramolecular interactions. In spite of being considered as ‘hard matter’ themselves, internal voids present in zeolites remain ‘soft matter’ and a parallel can therefore be drawn with enzymes found in Nature.

In the present communication, we aim to present our recent findings on zeolite synthesis in the presence of biomass or its extracted main building blocks. **Figure 1** illustrates the associated concept of Bio-Sourced Secondary Template “BSST” [4,5]. Structure-activity relationships were established between textural/structural properties of as-obtained biomass-mediated materials and their behaviour in C<sub>1</sub> chemistry: (i) CO<sub>2</sub> capture; (ii) conversion of methanol into hydrocarbons.



**Fig. 1.** Illustration of the Bio-Sourced Secondary Template concept.

## References

- [1] J.M. Lehn, *Science* **1985**, 227, 849.  
 [2] P. Mothe-Esteves, M.M. Pereira, J. Arichi, B. Louis, *Cryst. Growth & Des.* **2010**, 10, 371.  
 [3] S. Mintova, M. Jaber, V. Valtchev, *Chem. Soc. Rev.* **2015**, 44, 7207.  
 [4] Y. Zhang, B. Louis, *Microporous Mesoporous Mater.* **2023**, 350, 112431.  
 [5] Q. Zheng, B. Louis, *ChemCatChem* **2023**, 15, e202300210.



**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

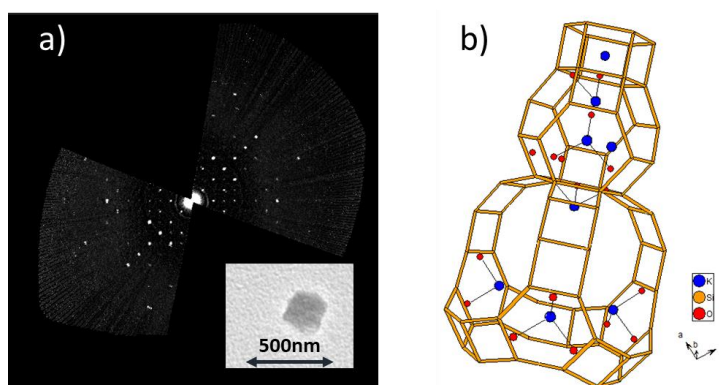
**3D ED pour la localisation des cations dans des faujasites échangées**

Y.-M. Chaib-Draa, T. Ors, I. Déroche, J.-L. Paillaud

<sup>a</sup> Université de Haute-Alsace, CNRS, IS2M UMR7361, F-68100 Mulhouse, France

<sup>b</sup> Université de Strasbourg, France

La nature et la disposition des cations au sein des zéolithes exercent une influence significative sur leurs propriétés physico-chimiques. La localisation précise de ces cations s'avère souvent complexe en raison de la petite taille des cristaux de zéolithe, restreignant ainsi l'application de techniques telles que la diffraction des rayons X sur monocristal. De même, la méthode Rietveld peut parfois se révéler difficile, voire impossible. Une solution prometteuse à ces problèmes est la diffraction électronique en mode tomographique (3D ED) avec précession des électrons sur microscope électronique en transmission (MET). Cette approche surmonte ces obstacles grâce aux progrès technologiques récents et au développement de programmes dédiés, lesquels réduisent de manière significative les effets dynamiques résultant des interactions entre les électrons et la matière [1]. Récemment, nous avons appliqué la technique 3D ED à une faujasite Y nanométrique, synthétisée par voie hydrothermale [2]. La résolution structurale obtenue grâce à la technique 3D ED, pour la forme sodique puis échangée avec  $K^+$ ,  $Mg^{2+}$  et  $Ca^{2+}$ , nous a permis de localiser précisément ces différents cations. La Figure 1 présente la distribution des  $K^+$  sur les positions I, I' et II dans K-Y [3].



**Fig. 1.** (a) Section  $h0l$  reconstituée de l'espace réciproque. En insert, cliché du cristal de K-Y utilisé pour la collecte des données. (b) Distribution des cations dans la zéolithe K-Y déterminée par 3D ED.

Références:

- [1] M. Gemmi, *et al.*, *Crystal Engineering and Materials*, 2019, vol. 75, no 4, p. 495-504.  
 [2] M. Borel, *et al.*, *New Journal of Chemistry*, 2017, vol. 41, no 22, p. 13260-13267. 345-352.  
 [3] Y.-M. Chaib-Draa, T. Ors, I. Déroche, J.-L. Paillaud, *en préparation*.



## Unveiling closed and open site stability of Sn-, Ti-, Hf-, and Zr-Beta zeolites: A DFT investigation for biomass sugar conversion

N. Abidi<sup>a</sup>, Y. Boudjema<sup>a</sup>, C. Chizallet<sup>a</sup>, K. Larmier<sup>a</sup>

<sup>a</sup> IFP Energies nouvelles, Rond-point de l'échangeur de Solaize – BP 3 69360 Solaize, France

\* [nawras.abidi@ifpen.fr](mailto:nawras.abidi@ifpen.fr)

Zeolites are highly efficient catalysts due to their unique nano-porous structures. By substituting Al with Sn, Ti, Zr, or Hf, we achieve distinct Lewis acidic properties, facilitating the conversion of carbohydrates like glucose, fructose, and xylose into furan compounds and organic acids.<sup>1</sup> Employing density functional theory (VASP, PBE-D2 density functional), our research investigates stability, Lewis acidity, and sugar adsorption in Sn-, Ti, Hf-, and Zr-Beta zeolites (modelled on polymorph B). First-principles thermodynamics was used to construct phase diagrams (Fig. 1), revealing the predominance of stable closed sites at low pressure (P) and high temperature (T). Our findings also offer novel insights into water adsorption in zeolites with respect to earlier proposals by favoring scenarios with undissociated H<sub>2</sub>O. The evaluation of Lewis acidity, quantified by pyridine adsorption, reveals various acidity levels across different T sites, with T6 showing the strongest and T9 the weakest Lewis acidity. Ti is identified as having the lowest Lewis acidity among the studied dopants. Expanding our study, we delve into glucose, fructose, and xylose adsorption. Our analysis consistently favors cyclic tautomers over linear forms, regardless of the specific T site or metal type. Intriguingly, Hafnium (Hf) emerges as the strongest adsorbent. Dispersion forces significantly contribute to adsorption energy, emphasizing their role in sugar-zeolite interactions. Current research addresses the computation of reaction pathways for the transformation of sugars. This study improves the molecular understanding of zeolite stability and catalytic behavior, providing valuable insights for the development of advanced catalysts in sustainable chemical processes.

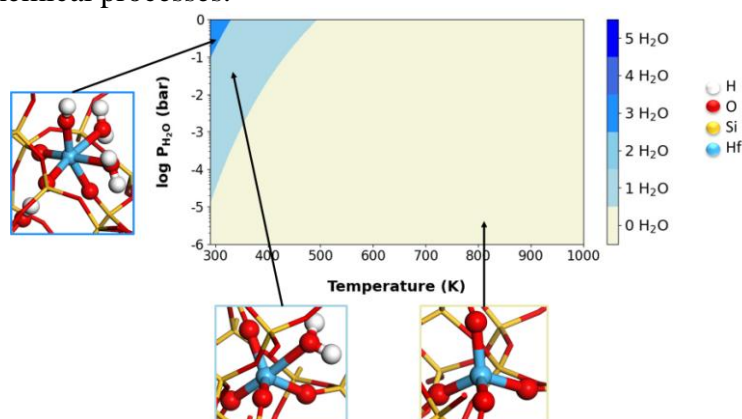


Fig. 1. Example of stability diagram of T1-Hf as function of T and P

### References

1. Luo, H. Y., Lewis, J. D., & Román-Leshkov, Y. *Annu Rev Chem Biomol Eng.* **2016**, 663-692.

**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

**Theoretical Study of the Steric Hindrance Effects on Pyridine Derivatives  
Adsorption in H-ZSM5 Zeolite**

Martine Castellà-Ventura<sup>a</sup>, Alain Moissette<sup>b</sup>, Emile Kassab<sup>a</sup>

<sup>a</sup> *Laboratoire de Chimie Théorique, UMR 7616 CNRS, Sorbonne Université, 4 place Jussieu, 75252 Paris, France.*

<sup>b</sup> *Laboratoire de Spectroscopie pour les Interactions, la Réactivité et l'Environnement, UMR 8516 CNRS, Université de Lille – Sciences et Technologies, 59655 Villeneuve d'Ascq, France.*

The theoretical study of the adsorption of pyridine (PY) and some of its alkylated derivatives (2-méthyl, 3-méthyl, 4-méthyl, 2,6-diméthyl, 2,6-méthylethyl, 3,5-diméthyl, 2,6-di(terbutyl) and 2,6-di(isobutyl) –pyridines) on different Brønsted acid sites (BAS) of H-ZSM-5 zeolite cavity by cluster model, using PBE functional including Grimme's empirical dispersion correction D3 in the density functional theory (DFT) calculations has been investigated. In this study a cluster model of 34 tetrahedral centers (34T) extracted from the straight channel of a siliceous crystallographic ZSM-5 structure has been used.

The substitution of one Si atom in different tetrahedral crystallographic T-sites by an aluminum atom within the ZSM-5 cavity has been considered. The confinement effects resulting from van der Waals dispersion interactions and steric constraints on the energetic and vibrational properties of adsorption complexes formed in the straight channel of H-ZSM-5 have been thoroughly examined.

Our DFT-D calculation results clearly show that upon adsorption of any PY derivative, a proton transfer occurs spontaneously from BAS of the zeolite to adsorbed molecule leading directly to the formation of a zwitterionic complex, as in the case of PY [1-2].

Whatever the adsorption complex, the calculated structures reflect a compromise between the repulsive interactions due to steric hindrance and the attractive van der Waals dispersion interactions between the atoms of the adsorbed molecule and those of the wall zeolite cluster.

Although the alkylated pyridine derivatives are distinguished by their steric hindrance, the energetic characteristics of the adsorption complexes are almost identical, consistent with their proton affinity, with the exception of 2,6-di(ter-butyl)-pyridine. In the complex involving the latter compound, the increase in dispersion forces is not enough to compensate for the strong steric hindrance, which explains the low adsorption energy.

Whatever the adsorbed molecule, the calculated vibrational frequencies and frequency shifts are in satisfactory agreement with the experimental results available in the literature.

**Références**

- [1] M. Castellà-Ventura, A. Moissette, E. Kassab, *Phys. Chem. Chem. Phys.* 20 (2018) 6354-6364.  
[2] M. Castellà-Ventura, A. Moissette, E. Kassab, *Computation* 8 (2020) 81.



**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

**Direct Visualisation of the Flexibility of RHO Nanozeolite**

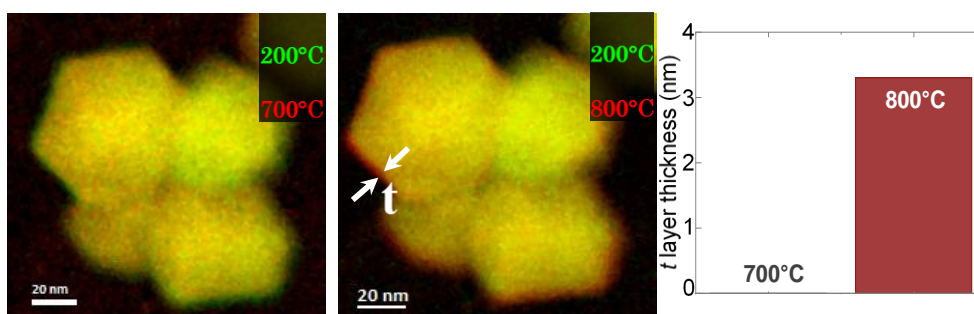
E. B. Clatworthy<sup>a\*</sup>, S. Moldovan<sup>b</sup>, K. Nakouri<sup>b</sup>, S. P. Gramatikov<sup>c</sup>, F. Dalena<sup>a</sup>, M. Daturi<sup>a</sup>, P. St. Petkov<sup>c</sup>, G. N. Vayssilov<sup>c\*</sup>, and S. Mintova<sup>a\*</sup>

<sup>a</sup> ENSICAEN, UNICAEN, CNRS, Laboratoire Catalyse et Spectrochimie (LCS), Normandie Université, 14050 Caen, France

<sup>b</sup> CNRS, INSA Rouen Normandie, Groupe de Physique des Matériaux UMR 6634, Université Rouen Normandie, F-76000 Rouen, France

<sup>c</sup> Faculty of Chemistry and Pharmacy, University of Sofia, 1126, Sofia, Bulgaria

Structural flexibility is an intrinsic feature of zeolites. Understanding the adsorbate-temperature relationships and their structural influence on zeolites is central to their optimisation and implementation as physical adsorbents, because of the significant temperature variations that can occur in separation processes due to the exothermic nature of CO<sub>2</sub> adsorption. Here we combine *in situ* variable temperature TEM analysis under different types of atmospheres (CO<sub>2</sub> and Ar), *operando* FTIR spectroscopy, and quantum chemical modelling of the zeolite framework and extra-framework cations to explore the structural flexibility behaviour of RHO nanozeolite.



**Fig. 1.** Superimposed micrographs acquired at different temperatures show the volume expansion of the crystals during the thermal treatment under CO<sub>2</sub> environments. Grain expansion as measured from the superposition of the micrographs acquired at different temperatures and denoted by *t*.

Analysis by 2D STEM-HAADF, electron tomography and EDS afforded the first volume rendering and 3D mapping of a high-aluminium nanozeolite, verifying the homogeneous distribution of elements throughout the discrete zeolite nanoparticles (~67 nm). Electron microscopy under different atmospheres (Ar vs CO<sub>2</sub>) and variable temperature 200–800 °C revealed the direct visualisation of the RHO nanozeolite structural flexibility behaviour, exemplified by the expansion of the discrete nanocrystals in response to different gases and temperatures (**Fig. 1**). Complementary *operando* FTIR spectroscopic analysis under similar conditions allowed us to follow the nature of the adsorbed CO<sub>2</sub> species within the zeolite micropores as well as revealing a clear evolution of the zeolite structural (T–O–T) bands with temperature. The use of quantum chemical modelling of the RHO framework and extra-framework cations demonstrated different flexibility behaviour of the zeolite in response to temperature in the presence or absence of CO<sub>2</sub>; this was found to be related to the greater oscillatory displacement of the Cs<sup>+</sup> extra-framework cations within the zeolite microporosity which affects their interaction with the zeolite framework.

**Références**

Clatworthy, E. B.; Moldovan, S.; Nakouri, K.; Gramatikov, S. P.; Dalena, F.; Daturi, M.; Petkov, P. S.; Vayssilov, G. N.; Mintova, S. *J. Am. Chem. Soc.*, **145**, 15313–15323, 2023



# POSTERS

## THEME 1


**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

**OSDA-free synthesis of ZSM-5 nanosheets with short b-thickness**

Qiudi Yue,<sup>a</sup> Honghai Liu<sup>b</sup>, Zhengxing Qin<sup>c</sup>, Svetlana Mintova<sup>a,c</sup>

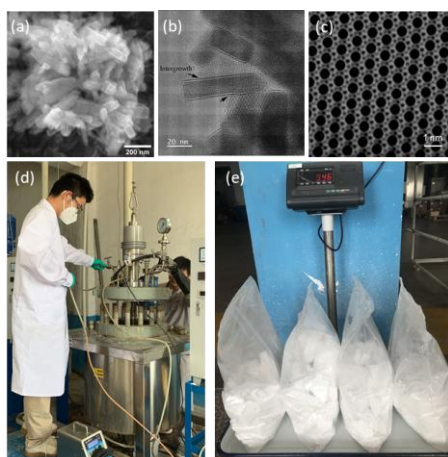
<sup>a</sup> *Laboratoire Catalyse et Spectrochimie (LCS), CNRS, 14050 Caen, France*

<sup>b</sup> *Petrochemical Research Institute, PetroChina, 730060 Lanzhou, China*

<sup>c</sup> *College of Chemical Engineering, China University of Petroleum (East China), Qingdao, China*

ZSM-5 zeolite with MFI type framework structure is the core catalyst in many important industrial processes owing to its shape selectivity. However, its molecule-level channels impose a significant restriction on the transport of molecules within crystals, resulting in slow reaction kinetics, an increase in the secondary reactions and a subsequent catalyst deactivation by coking. Therefore, great efforts have been dedicated to develop ZSM-5 catalysts to overcome the diffusional limitations by introducing of secondary meso-/macro-pores and decreasing of crystal size to nano dimensions. Considering the anisotropic diffusion of molecules in two channels of MFI zeolite, the diffusion in the sinusoidal channels is much slower than in the straight ones. Therefore, ZSM-5 nanosheets with short b-axis thickness (short straight channel) are highly desired towards reduction of diffusion resistance. However, the design and development of eco-friendly synthesis protocols with low-cost and high efficiency in the absence of organic templates remain elusive.

In this work, our recent results on new methodologies for OSDA-free synthesis of ZSM-5 nanosheets with tunable short *b*-axis thickness will be presented. The utilization of additives and seeds for the preparation of ZSM-5 nanosheets was systematically studied and the synthetic conditions including silica and alumina sources, type of seeds, and alkalinity were optimized. As a result, controllable *b*-thicknesses ranging from 20-200 nm of ZSM-5 zeolites were achieved in the absence of organic templates. The synthesis procedure for ZSM-5 nanosheets was scaled up from several grams (lab-scale) to several kilograms (industrial scale); the properties of the materials were identical.



**Fig. 1.** (a) SEM, (b) TEM, and (c) simulated iDPC-STEM images of ZSM-5 nanosheets; (d) industrial scale autoclave and (e) product yield of 50L scale-up synthesis

**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

**Synthesis of Faujasite from natural clay via high-pressure hydrothermal method**

**S.B. Gambo**, N.P. Martin, C. Chassigneux, N. Dairou, V. Wernert

*Aix-Marseille University, CNRS, MADIREL UMR 7246, 13397 Marseille Cedex 20, France*

The synthesis of zeolites from natural clay minerals represents a promising avenue for the sustainable production of environmentally friendly and relevant industrial adsorbents as clays are abundant and widely distributed geological resources [1]. In this study, we report the transformation of clay (kaolinite type) into faujasite zeolite (FAU X) through a carefully controlled high-pressure (hp-) hydrothermal method (1 kbar H<sub>2</sub>O pressure) at different gradients of temperature in high pressure autoclaves. The hp-hydrothermal method uses water as the solvent and the reaction medium is in a closed system [2, 3]. The kaolinite was first transformed to metakaolinite via thermal treatment. Sources of silica and sodium hydroxide were added to respectively adjust the Si/Al ratio and the charge compensation. Hydrothermal reactions were performed at 1 kbar to obtain well crystallized FAU X. The samples were characterized using powder X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Energy-Dispersive X-ray Spectroscopy (EDS), and nitrogen adsorption-desorption isotherms at 77 K. These analyses provide insights into the crystal structure, morphology, elemental composition, and surface area and porosity of the synthesized FAU X. The impact of synthesis parameters, such as temperature, time, pressure, and varying concentrations of the alkaline solution, on the final product was systematically investigated to help tailor the zeolite's properties meet specific application requirements. This environmentally conscious use of clay as a starting material and the transformative potential of the hp-hydrothermal method in sustainable zeolite production does not only contribute to the development of eco-friendly zeolites but also underscores great potential of the hp-hydrothermal method in the realm of zeolite research aligning with the global push for greener and more responsible technological advancements.

- [1] O. O. Ltaief, S. Siffert, C. Poupin, S. Fourmentin, and M. Benzina, "Optimal Synthesis of Faujasite- Type Zeolites with a Hierarchical Porosity from Natural Clay," *Eur J Inorg Chem*, vol. 2015, no. 28, pp. 4658–4665, Oct. 2015, doi: 10.1002/ejic.201500537.
- [2] V. Wernert *et al.*, "Cancrinite synthesis from natural kaolinite by high pressure hydrothermal method: Application to the removal of Cd<sup>2+</sup> and Pb<sup>2+</sup> from water," *Microporous and Mesoporous Materials*, vol. 301, p. 110209, Jul. 2020, doi: 10.1016/j.micromeso.2020.110209.
- [3] H. Ghobarkar, O. Schäf, and P. Knauth, "Zeolite Synthesis by the High-Pressure Hydrothermal Method: Synthesis of Natural 6-Ring Zeolites with Different Void Systems," *Angewandte Chemie International Edition*, vol. 40, no. 20, pp. 3831–3833, 2001, doi: 10.1002/1521-3773(20011015)40:20<3831::AID-ANIE3831>3.0.CO;2-Z.



## 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

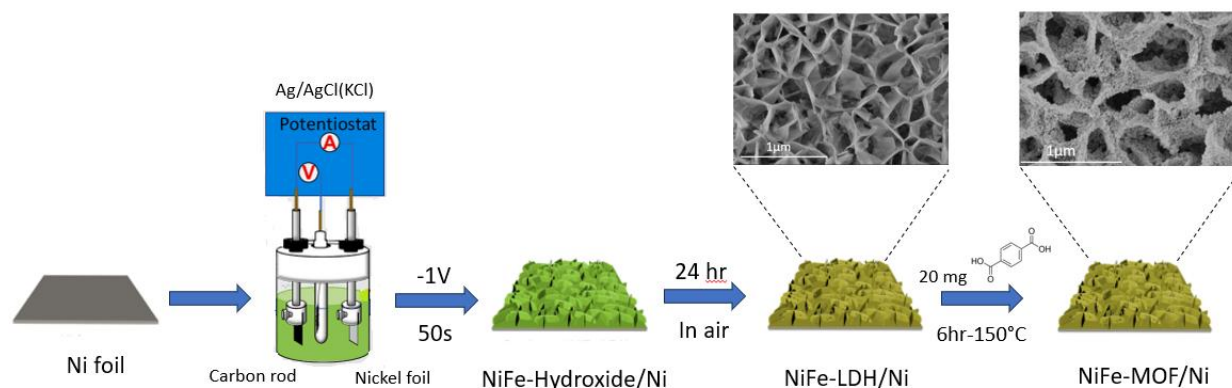
## In situ transformation of layered double hydroxide arrays into 2D Metal Organic Framework for oxygen evolution reaction

Y. Smati,<sup>a</sup> M. Turmine<sup>a</sup> V. Vivier,<sup>a</sup> J. Reboul<sup>a</sup> J. Blanchard<sup>a</sup>

<sup>a</sup> Laboratoire de Réactivité de Surface (LRS), CNRS, UMR 7197, Sorbonne Université, Paris, France

### Abstract

Oxygen evolution reaction is one of the most important reactions in the field of energy storage and conversion. It is indeed involved in the process of water splitting and metal-air batteries and new catalysts, combining high densities of active sites and high surface area are needed. In this context, monometallic and bimetallic Metal-Organic Frameworks (MOF) were recently shown to be promising catalysts<sup>1</sup>. Herein, we demonstrate an original strategy to homogeneously cover an electrode consisting of a Ni foil with hierarchical structures of MOF nanocrystals. First, a fast electrodeposition step at -1V vs Ag/AgCl allowed us to synthesize sulfated NiFe-LDHs as thin layers of smooth nanosheets arrays (**Figure 1**). These LDH nanosheets were then used as preformed metal precursors to synthesize ultrathin rough NiFe-MOF nanosheet arrays on Ni Foil (NS/NF) using a solvothermal treatment in the presence of terephthalic acid (BDC)<sup>2,3</sup>. XRD analysis shows the formation of a MOF (CCDC 985792, Ni<sub>2</sub>(OH)<sub>2</sub>(C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>)) with a lamellar structure, whereas Raman and ATR-IR spectra confirm the total conversion of LDH into MOF. Interestingly, SEM analysis shows that the sheet-shape of the parent LDH was preserved after its conversion into MOF, leading to a hierarchical structure composed of MOF nanocrystals homogeneously covering the Ni foil (**Figure 1**). EDX analysis, as well as XPS analyses confirmed the existence of both Ni and Fe within the MOF crystals. Both the precursor composed of NiFe-LDH and the NiFe-MOF materials were used as electrocatalysts for OER with the aim to establish the relationship structure-activity.



**Fig. 1.** Synthesis of NiFe-LDH and NiFe-MOF nanosheets arrays

### References

- (1) Wang, C.; Lin, Y.; Cui, L.; Zhu, J.; Bu, X. 2D Metal–Organic Frameworks as Competent Electrocatalysts for Water Splitting. *Small* **2023**, *19* (15), 2207342. <https://doi.org/10.1002/sml.202207342>.
- (2) Li, Z.; Shao, M.; An, H.; Wang, Z.; Xu, S.; Wei, M.; Evans, D. G.; Duan, X. Fast Electrosynthesis of Fe-Containing Layered Double Hydroxide Arrays toward Highly Efficient Electrocatalytic Oxidation Reactions. *Chem. Sci.* **2015**, *6* (11), 6624–6631. <https://doi.org/10.1039/C5SC02417J>.
- (3) Liu, Y.; Li, X.; Sun, Q.; Wang, Z.; Huang, W.-H.; Guo, X.; Fan, Z.; Ye, R.; Zhu, Y.; Chueh, C.-C.; Chen, C.-L.; Zhu, Z. Freestanding 2D NiFe Metal–Organic Framework Nanosheets: Facilitating Proton Transfer via Organic Ligands for Efficient Oxygen Evolution Reaction. *Small* **2022**, *18* (26), 2201076. <https://doi.org/10.1002/sml.202201076>.



## 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

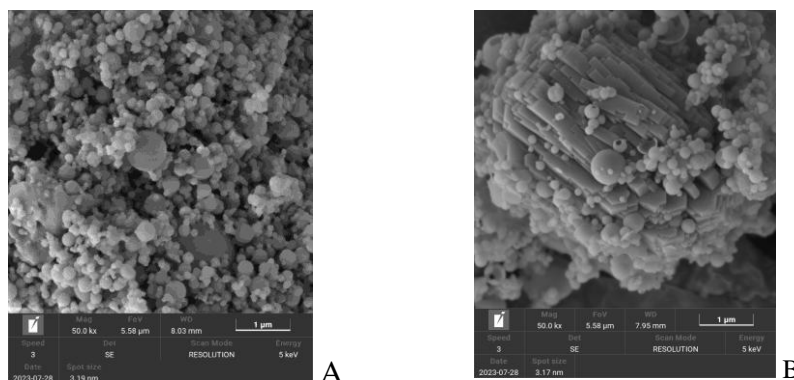
### Synthesis of ZSM-5 from Si residues of solar panel production

Oliveira, R. S. R.<sup>a</sup>, Bieseki, L.<sup>a,b</sup> and Pergher, S. B.C.<sup>a</sup>

<sup>a</sup> LABPEMOL – Universidade Federal do Rio Grande do Norte, UFRN, Brasil

<sup>b</sup> IC2MP - Institut de Chimie des Milieux et Matériaux de Poitiers, France.

With the context of exploiting renewable energy sources the production of solar panels massively increased in recent years. During the production of these metallic Si panels a residue features a large amount of SiO<sub>2</sub> (95%) is obtained as waste product. The synthesis of zeolites from waste is a currently widely investigated research field. As such the use of coal ash<sup>[1]</sup>, spodumene<sup>[2]</sup>, and clays<sup>[3]</sup>, *etc.* as alternative sources of Si and Al in the production of zeolites has been described. In this communication we present a new synthetic route for producing ZSM-5 zeolite using Si waste generated in the production of solar panels based on metallic silicon as a source of silica. The synthesis was carried out in a basic medium using an organic director for seed production. Crystallization kinetics were measured. It was found that the residue partially remains present in the final zeolitic material. It is further interesting to note that at high crystallization times the apparition of a lamellar phase can be distinguished in XRD patterns, TEM and SEM (**Figure 1**).



**Fig. 1:** SEM images of the products obtained after 6 h (A) and 24 h (B) of crystallization time.

## Références

- [1] J.D.C. Izidoro, D. Alves, S. Fernando, S. Wang, Characteristics of Brazilian coal fly ashes and their synthesized zeolites, *Fuel Process. Technol.* 97 (2012) 38–44.
- [2] L. Bieseki, D.B. Ribeiro, E. V. Sobrinho, D.M.A. Melo, S.B.C. Pergher, Síntese de zeólitas utilizando resíduo sílico-aluminoso proveniente do processo de extração de lítio, *Cerâmica.* 59 (2013) 466–472.
- [3] M. Anbia, E. Koohsaryan, A. Borhani, Novel hydrothermal synthesis of hierarchically-structured zeolite LTA microspheres, *Mater. Chem. Phys.* 193 (2017) 380–390..

**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

## Elaboration de matériaux composites MOF A520/polymères pour l'adsorption de l'humidité ambiante

M. Froehly,<sup>a,b</sup> G. Chaplais,<sup>b</sup> H. Nouali,<sup>b</sup> V. Roucoules,<sup>b</sup> P. Forler,<sup>a</sup> T. J. Daou<sup>a</sup>

<sup>a</sup> APTAR CSP Technologies, Niederbronn les Bains

<sup>b</sup> Institut de Science des Matériaux de Mulhouse (IS2M), Université de Haute Alsace (UHA), Université de Strasbourg (UniStra), CNRS, IS2M UMR 7361, Mulhouse

Dans l'industrie pharmaceutique, la contamination moléculaire est une problématique majeure car elle peut affecter la qualité et la performance d'un médicament. Selon les conditions de stockage, l'humidité atmosphérique peut accélérer les processus de dégradation de ces derniers. Ainsi, pour augmenter la durée de conservation de ces produits, APTAR CSP Technologies a développé des formulations dites 3 phases (polymère principal + polymère secondaire + adsorbant) dont l'adsorbant est la zéolithe de type structural LTA (4A) qui a la propriété d'adsorber l'humidité [1]. Ces formulations sont utilisées pour la fabrication par extrusion/injection d'emballages pharmaceutiques. Cependant, leur efficacité vis-à-vis de l'humidité est limitée par la capacité d'adsorption de la zéolithe 4A (254,4 mg<sub>eau</sub>/g<sub>zéolithe 4A</sub>). L'objectif de cette étude est de substituer dans la formulation cette zéolithe 4A par un MOF (Metal-Organic Framework) hydrophile possédant une capacité d'adsorption en eau supérieure. Parmi les MOFs hydrophiles reportés dans la littérature, le MOF A520 apparaît comme un excellent candidat (stabilité thermique, coût de production, capacité d'adsorption avec 452,0 mg<sub>eau</sub>/g<sub>MOF A520</sub>) [2]. Ce MOF a donc été incorporé avec différents taux de charge (30 à 55 %) dans des formulations 3 phases à la place de la zéolithe, pour la production de granulés, de films et de pièces moulées (Fig.1). Des mesures d'adsorption de vapeur d'eau à 22 °C et 80 % d'humidité relative en chambre climatique ont montré que les composites MOF A520/polymères présentent des capacités d'adsorption en vapeur d'eau nettement supérieures à celles des composites zéolithe 4A/polymères.

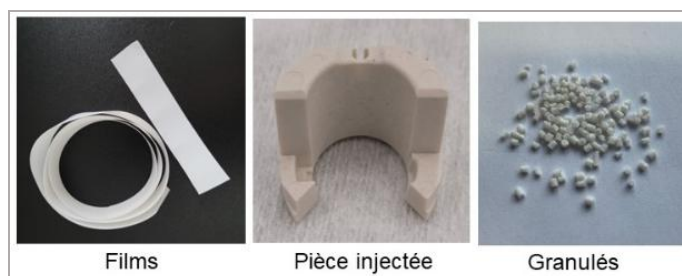


Fig. 1. Photographies des différentes mises en forme réalisées avec le MOF A520

[1] Tahraoui, Z.; Nouali, H.; Marichal, C.; Forler, P.; Klein, J.; Daou, T. J. *Molecules*, **26**, 4815 (2021)

[2] Kayal, S.; Chakraborty, A.; Teo, H. W. B. *Mater. Lett.*, **221**, 165-167 (2018)



## 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

## Préparation de (Fe,Ti,Ni)/ZSM-5 à partir d'argiles naturelles et application à la dégradation de contaminants organiques

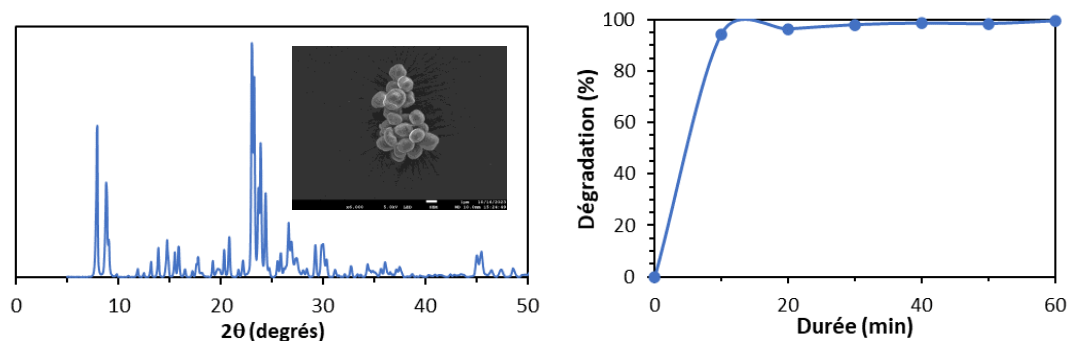
Koffi Siméon KOUADIO,<sup>a,b</sup> Tchirioua EKOU,<sup>a</sup> Jérémy DHAINAUT<sup>b</sup>

<sup>a</sup> Université Nangui Abrogoua, LTPCM Bp 801 Abidjan 02, Côte d'Ivoire

<sup>b</sup> UMR 8181 – UCCS – Unité de Catalyse et Chimie du Solide, F-59000 Lille, France.

Les zéolithes sont considérées comme des matériaux prometteurs pour l'élimination de contaminants organiques émergents contenus dans l'eau, principalement par piégeage. Elles présentent de nombreux avantages du fait de leur grande stabilité, leur capacité d'échange ionique et leurs propriétés texturales d'intérêt liées à leur structure microcristalline. Leur synthèse peut être réalisée à partir de précurseurs commerciaux, ou à partir d'argiles naturelles présentant l'intérêt d'un coût moindre et d'une plus grande disponibilité locale.

Au cours de ce travail, des zéolithes de type MFI ont été synthétisées par voie hydrothermale à partir de l'argile de boule du type kaolin provenant de la région de l'Agnébi (Côte d'Ivoire). Plusieurs oxydes métalliques ( $\text{TiO}_2$ ,  $\text{FeO}_x$ ,  $\text{NiO}$ ) ont été déposés *in-situ*, et les matériaux résultants ont été utilisés pour l'adsorption et la photodégradation du bleu de méthylène (MB) et du chloridazone. La DRX en **Figure 1.A** nous montre que tous les matériaux sont bien cristallisés et de type structural MFI. Des raies additionnelles, relatives à la présence d'oxydes métalliques, sont rarement observées et restent dans ces cas larges. Par MEB, les particules sont maclées et de forme pseudo-sphérique, composées de cristallites agglomérées. En **Figure 1.B**, un exemple de cinétique de dégradation du MB (50  $\mu\text{g/L}$ ) est proposé. Sa photodégradation dans l'eau en présence de Fe/ZSM-5 est rapide (< 30 minutes). Nous nous intéressons désormais à l'effet de la mésoporisation de la zéolithe.



**Figure 1** : DRX et cliché MEB de la zéolithe Fe/ZSM-5 (A), et cinétique de dégradation du MB (B).



---

**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

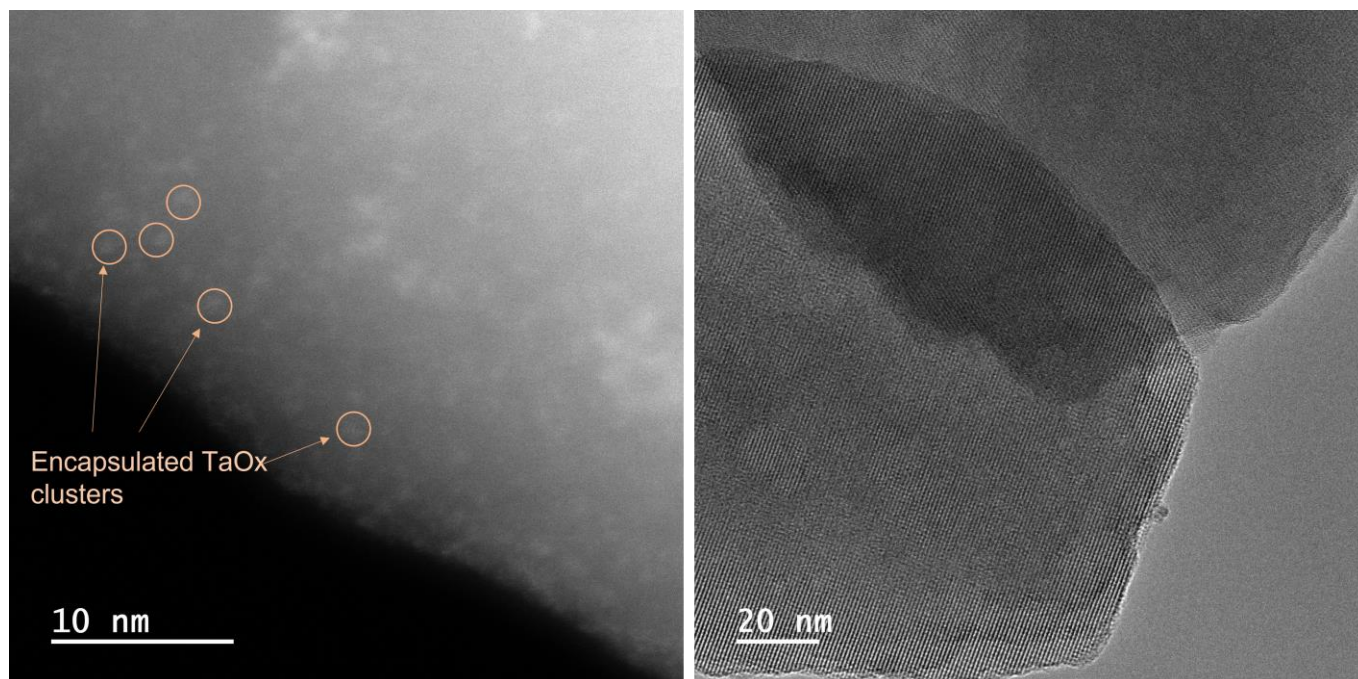
***Encapsulation of metallic oxide aggregates in siliceous materials*****R. DEL CERRO, G. PIRNGRUBER, N. CADRAN***IFP Energies nouvelles, Rond-point de l'échangeur de Solaize – BP 3 69360 Solaize, France*

Biobased alcohols like bio-ethanol can be converted to a number of very interesting chemicals. Many of these transformations involve MPV oxidation reactions, catalysed by Lewis acids, followed by aldol condensation reactions, which can be acid or base catalyzed. However, the presence of Bronsted acid sites is highly undesirable because they will cause unwanted side reactions. Lewis acidic zeolites are very interesting catalysts because the pore topology of the zeolite can influence the selectivity, but it is challenging to incorporate and stabilize Lewis acidic heteroatoms in the zeolite pores, while completely avoiding the formation of Bronsted acidity. We were specifically interested in Tantalum as Lewis acid. The present paper describes methods to prepare small encapsulated Tantalum oxide clusters (TaO<sub>x</sub>@zeolithe). Both the effect of the structure (pore size and topology), morphology (crystals size) and of the active sites (dispersion, location, acid strength) were studied. The activity and stability of the catalysts were evaluated in Lewis acid catalyzed test reactions.

TaO<sub>x</sub>@BEA was prepared by excess impregnation on a previously dealuminated commercial Beta zeolite (Zeolyst CP814E; Si/Al=13)<sup>1</sup>. TaO<sub>x</sub>@MFI zeolite samples were made by direct synthesis<sup>2</sup>. In this synthesis, the challenge was to control the formation of Tantalum based clusters in the basic synthesis medium. The impact of different parameters like the use of chelating agents for tantalum species, the addition of Na were studied. Solids were characterized by XRD, N<sub>2</sub> physisorption and TEM. Active phase dispersion and distribution were characterized by STEM, IR-pyridine. A good dispersion of tantalum oxide sites was obtained, even at high loadings (6.8% m of Ta<sub>2</sub>O<sub>5</sub>). The modification of the synthesis parameters allowed us to get different particles morphologies while maintaining an excellent dispersion.

To evaluate the performances of the synthesized catalysts we conducted different reactions involving the Lewis acidity like a MPV (Meerwein-Ponndorf-Verley) cyclohexanone reduction by isopropanol. Promising results were obtained showing good Lewis acid character. Activity and selectivity were greatly influenced by crystals pore sizes and active phase dispersion.





**Fig. 1.** HAADF-STEM (left) and MET (right) images of the as-synthesized Ta (Silicalite-1) (5.6% w).

#### Références

- [1] Dzwigaj S., Millot Y., Che M. Ta(V)-Single Site BEA Zeolite by Two-Step Postsynthesis Method: Preparation and Characterization, *Catalysis Letters*, 2010, **135**, 3-4, 169-174. DOI: 10.1007/s10562-010-0284-5.
- [2] Yuan E., Dai W., Wu G., Guan N., Li L. Entrapped NbOx clusters in MFI zeolite for sustainable acid catalysis, *Microporous and Mesoporous Materials*, 2020, **305**, 110361. DOI: 10.1016/j.micromeso.2020.110361.


**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

## Explore solid-state synthesis in the quest of achieving Zeolite-Templated Carbons

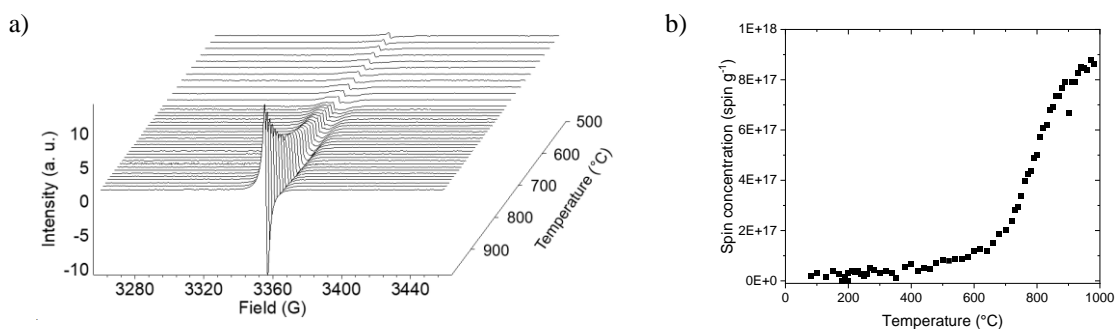
S. Compère<sup>a</sup>, A. Moissette<sup>b</sup>, I. Batonneau-Gener<sup>a</sup>, A. Sachse<sup>a</sup>

<sup>a</sup> Institut de Chimie des Milieux et Matériaux de Poitiers, IC2MP UMR 7285, 4 Rue Michel Brunet 86073 POITIERS CEDEX 9, France.

<sup>b</sup> Laboratoire de Spectroscopie pour les Interactions la Réactivité et l'Environnement Université de Lille, UMR CNRS 8516-LASIRE, 59000 Lille, France

Zeolite-Templated Carbons (ZTCs) are nanostructured and highly porous carbon materials obtained through negative replication of zeolites by using gaseous or liquid carbon precursors. They show great promise for the development of energy storage and transformation devices due to their electrical conductivity and textural properties.[1]

Recently, a solid-state synthesis of Zeolite-Templated Carbons using anthracene as carbon precursor was elaborated. This approach allowed for achieving ZTCs with modified network properties.[2] In the quest to expand this approach to more flexible and functional precursors, the present contribution aims at presenting in which way the approach can be extended using solid carbon precursors with different chemical and structural properties. Hence, *trans*-stilbene, *para*-terphenyl and phenothiazine were directly combined with protonic Y zeolite. An *in situ* Electron Paramagnetic Resonance (EPR) study was carried out allowing to evidence different radical generation behaviours as a function of the carbon precursor and applied temperature. These radicals might play a pivotal role in ZTC formation.[3] Further insights on the chemical and textural properties were achieved by UV/vis and RAMAN spectroscopy, nitrogen physisorption at 77 K and XRD. Solid-state ZTC synthesis emerges as new gateway in the quest of designing functional microporous carbon materials.



**Fig. 1.** a) *In situ* EPR spectra of *trans*-stilbene@Y hybrid, b) Evolution of spin concentration as a function of the temperature.

**References**

- [1] H. Nishihara, T. Kyotani, *Chem. Commun.*, 54, 5648 (2018)  
 [2] T. Aumond, A. Le Person, I. Batonneau-Gener, H. Vezin, A. Sachse, A. Moissette, *J. Phys. Chem. C*, 127 (7), 3486-3496 (2023)  
 [3] T. Aumond, H. Vezin, I. Batonneau-Gener, S. Compère, Y. Pouilloux, A. Le Person, A. Moissette, A. Sachse, *Small*, 19, 2300972 (2023)



- 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

## THEME

# Enhancing CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> Separations through Partial Mg-Exchanged Gismondine

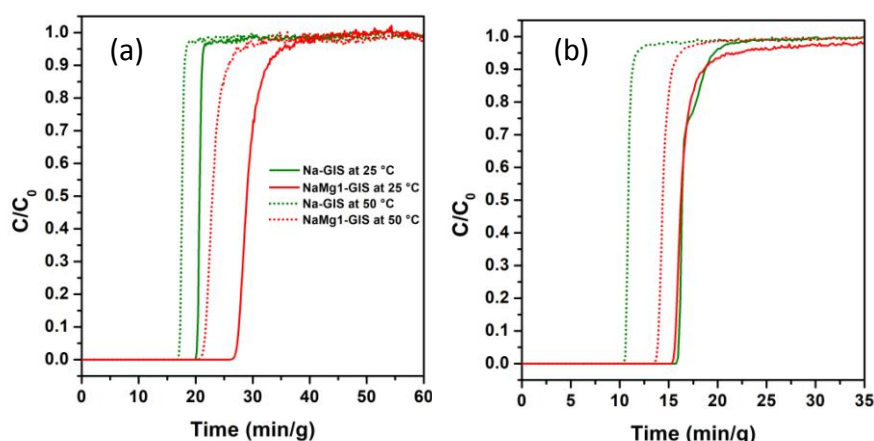
J. Al Atrach,<sup>a</sup> E. B. Clatworthy,<sup>a</sup> J. Rey,<sup>a</sup> Y. Xiong,<sup>a</sup> I. E. Golub,<sup>a</sup> A. Daouli,<sup>b</sup> M. Desmurs,<sup>a</sup> M. Badawi,<sup>b</sup> R. Guillet-Nicolas,<sup>a\*</sup> V. Valtchev<sup>a\*</sup>

<sup>a</sup> Université de Normandie, ENSICAEN, UNICAEN, CNRS, Laboratoire Catalyse et Spectrochimie (LCS), Caen, 14050, France

<sup>b</sup> Université de Lorraine, CNRS, Laboratoire de Physique et Chimie Théoriques (LPCT), Nancy, F-54000, France

The CO<sub>2</sub> adsorption performance of a zeolite is related to the framework structure and extra-framework composition.[1] In this context, the small-pore zeolite Gismondine, with its unique pore size and structure and easily replaceable charge-balancing cations, offers promises for efficient separation of small gas molecules, such as CO<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub>. [2] Herein, we investigate a new unexplored candidate for separating CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> gas mixtures, partially Mg-exchanged GIS with 30% and 50% exchange degrees, using complementary analyses, including static and dynamic adsorption experiments supported by DFT calculations.

The static adsorption experiments reveal the exceptional CO<sub>2</sub> adsorption capacity and selectivity of NaMg1-GIS with a lower Mg<sup>2+</sup> content (30%). Conversely, NaMg3-GIS, with higher Mg<sup>2+</sup> content (50%), demonstrated reduced CO<sub>2</sub> adsorption and lower selectivities due to restricted access to the pore network. DFT calculations supported these findings, showing stronger adsorption on Mg<sup>2+</sup> sites and revealing accessibility challenges in NaMg-GIS with higher Mg<sup>2+</sup> concentrations. Dynamic breakthrough curve analysis (**Fig. 1**) supported single-component adsorption results, highlighting NaMg1-GIS's superior CO<sub>2</sub> adsorption capacity and selectivity for CO<sub>2</sub> over N<sub>2</sub> and infinite CO<sub>2</sub>/CH<sub>4</sub> selectivity compared to the all-sodium GIS.



**Fig. 1:** CO<sub>2</sub> breakthrough curves at 25 and 50 °C obtained from competitive dynamic adsorption experiments, CO<sub>2</sub>/N<sub>2</sub>/He, 5/25/70 (a) and CO<sub>2</sub>/CH<sub>4</sub>/He, 20/30/50 (b).

## References

- [1] D. Fu et M. E. Davis, *Chem. Soc. Rev.*, vol. 51, n° 22, p. 9340- 9370, 2022.  
 [2] M. Fischer et R. G. Bell, *J. Phys. Chem. C*, vol. 116, n° 50, p. 26449- 26463, 2012.



Thème

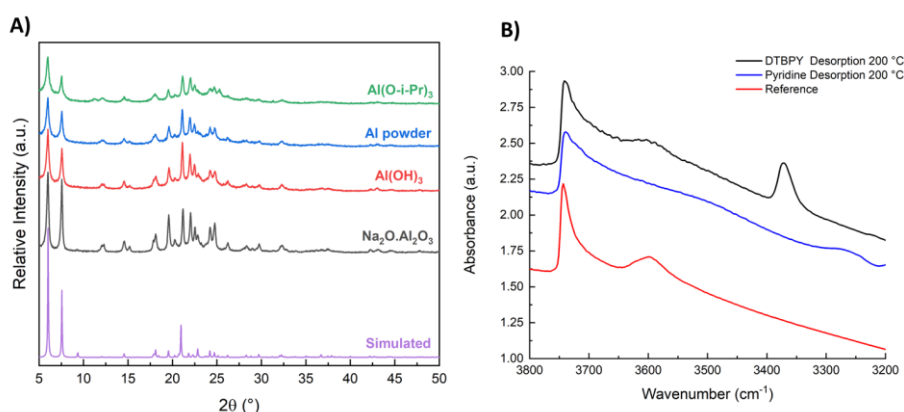
## Optimizing the synthesis and investigating acidic properties of UTD-1: a 14-membered ring aluminosilicate

M. Fahda<sup>a</sup>, A. Youssef<sup>a</sup>, L. Lakiss<sup>a</sup>, V. Valtchev<sup>a\*</sup>

<sup>a</sup> Laboratoire Catalyse et Spectrochimie (LCS), Normandie Université, ENSICAEN, UNICAEN, CNRS, Caen, 14050 (France)

\* [valentin.valtchev@ensicaen.fr](mailto:valentin.valtchev@ensicaen.fr)

In 1995, the UTD-1 (DON) discovery transformed zeolite synthesis by introducing extra-large pores[1], expanding catalytic potential. Despite the promise, direct aluminum incorporation posed a challenge. Two decades later, a new benzimidazole-based structure-directing agent (SDA) enabled aluminosiliceous UTD-1 synthesis[2], reigniting interest. The lack of *in situ* infrared spectroscopy for acid site characterization in the literature prompted our study. Considering the anticipated surge of interest in aluminosilicate UTD-1, this work comprehensively examines the diverse synthesis conditions involved in its preparation. We study their impact on synthesis duration, aluminum loading, crystal size, and morphology. Furthermore, we conduct *in situ* infrared spectroscopy studies on UTD-1, allowing us to determine the molar extinction coefficient of pyridinium ions interacting with UTD-1's Brønsted acid sites. Our preliminary results show that UTD-1 can be exclusively obtained over a broad range of initial Si/Al ratios and using different aluminum sources (Fig. 1A). Moreover, the choice of aluminum source has a detrimental effect on the size and shape of UTD-1 crystals. In our work, the acidic properties of a UTD-1 material with a Si/Al ratio down to 26 are reported for the first time. We show that pyridine can access most of the acid sites within UTD-1, unlike 2,6-ditert-butyl pyridine, which can access only around 30% of the acid sites (Fig. 1B). Furthermore, we determined the extinction coefficient of the pyridine at the 1545 cm<sup>-1</sup> adsorption to be 1.16 cm cm.μmol<sup>-1</sup> which permits the quantification of the concentration of Brønsted acid sites.



**Fig. 1. A) Powder x-ray diffraction patterns for UTD-1 synthesized using different aluminum precursors, and B) *in situ* infrared spectra for UTD-1 before and after Py and DTBPY adsorption.**

### References

1. Freyhardt, C., Tsapatsis, M., Lobo, R., Balkus, K. & Davis, M. A high-silica zeolite with a 14- tetrahedral-atom pore opening. *Nature* 381, 295–298 (1996).
2. Zi, W. W., Gao, Z., Zhang, J., Lv, J. H., Zhao, B. X., Jiang, Y. F., ... & Chen, F. J. 2019, *Microporous and Mesoporous Materials*, 290, 109654.

**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

**IN SITU ANCHORING OF TiO<sub>2</sub> NANOCRYSTALS IN THE STRUCTURE OF KIT-5 AND KIT-6 FOR PHOTODEGRADATION OF RHODAMINE B DYE**

Antony J. T. da Silva<sup>a</sup>, Larissa G. Ribeiro<sup>a</sup>, Aline E. B. Lima<sup>b</sup>, Geraldo E. L. Júnior<sup>b</sup>, Anne G. D. Santos<sup>a</sup>

<sup>a</sup> *Laboratório de Catálise, Ambiente e Materiais-LACAM/Departamento de Química./Universidade do Estado do Rio Grande do Norte - UERN, Mossoró-RN, Brasil.*

<sup>b</sup> *GrEEnTec-DQ, Universidade Estadual do Piauí-UESPI, Teresina-PI, Brasil.*

The treatment of effluents rich in organic compounds, such as dyes, from the textile industry, can be carried out through heterogeneous photocatalysis(1),(2). In this process, TiO<sub>2</sub> stands out due to its low cost and photostability, but it has some limitations, which are its particle size and its application in an aqueous medium, which when added to a mesoporous support are alleviated(3). The aim of the present work was to achieve *in situ* titania functionalized KIT-5 and KIT-6 materials by using a colloidal TiO<sub>2</sub> solution during *in situ* anchoring (ISA) method(4) and the use of these in the photodegradation of the Rhodamine B dye. The synthesis of materials followed the hydrothermal method(5),(6) with a silicon/titanium ratio of 25, where the incorporation of the titanium oxide occurred before adding the silicon source. After calcination, the materials were characterized through X-ray diffraction, proving the achievement of KIT-5 and -6. From X-ray fluorescence it was deduced that experimental molar ratio approached the theoretical value for both materials. The scanning electron microscopy images showed that material present expected morphology. High Ti distribution was determined by EDS. Photocatalytic tests proved for Rhodamine B dye degradation of 87.5% and 97.0% for KIT-5/TiO<sub>2</sub> and KIT-6/TiO<sub>2</sub>, respectively, as well as for high recyclability for successive cycles.

**Références**

1. C.R. Mendes, G. Dilarri, M.R. Stradioto, A.U. Faria, E.D. Bidoia, R.N, *Environ. Sci. Pollut. Res*, **2019**, 26.
2. C. Zhi Lin., X. L. Yan, L. Zan, *Ecotoxicology and Environmental Safety*, **2018**, 148585–592.
3. P. S. Basavarajappa, S. B. Patil, N. Ganganagappa, K. R. Reddy, A. V. Raghu, Ch. V. Reddy, *International Journal of Hydrogen Energy, Tamakuro*, Índia, **2019**, 45.
4. M. M. ARAÚJO, L. K. R. SILVA, J. C. SCZANCOSKI, M. O. ORLANDI, E. LONGO, A. G. D. SANTOS, L. S. CAVALCANTE. *Applied Surface Science*, **2016**, 389, 1137–1147.
5. K, Freddy, L, Dinan. A, Gopinathan M., P, In-Soo Park, S, Leonid A., S, Alexandr N., R. Ryong. **2003**. *J. Phys. Chem. B*, 107, 14296-14300
6. K, Freddy, C. H. Shin, R. Ryong. **2003**. *Chem. Commun.* p. 2136-2137.



## 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

### Swift sonohydrothermal synthesis of zeolite A

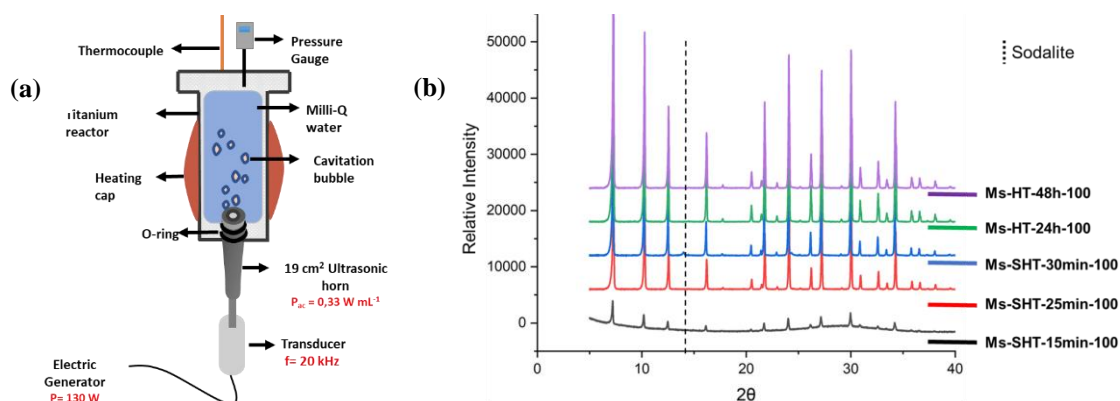
William's Nzodom<sup>1</sup>, Tony Chave<sup>1</sup>, Sabine Valange<sup>2</sup>, Sergey I. Nikitenko<sup>1</sup>

<sup>1</sup> Université de Montpellier, ICSM, UMR 5257 CNRS, CEA, ENSCM, Bagnols sur Cèze

<sup>2</sup> Université de Poitiers, CNRS, Institut de Chimie des Milieux et Matériaux de Poitiers, Poitiers

Sonochemistry (i.e. the use of ultrasound in chemical reactions) has emerged as an attractive approach for the synthesis of nanomaterials. Recent studies have highlighted the importance of ultrasonic treatment during the preparation of zeolite materials and its influence on the transformation kinetics of the crystalline phases during thermal treatment.

The aim of the present work was to investigate, for the first time, the simultaneous coupling of ultrasound and hydrothermal (HT) conditions for the synthesis of zeolite materials and mechanism thereof. Zeolite A was selected for that purpose. Its conversion into sodalite was also examined under these coupling conditions. The zeolite synthesis was carried out under sonohydrothermal (SHT) conditions using a reactor specially designed to allow the application of ultrasonic irradiation at 20 kHz in an autoclave-type reactor (Figure 1a) heated up to 200 °C under autogenous pressure [1]. The conversion kinetics of the amorphous gel to zeolite A and further to sodalite was examined. For this, the action of ultrasound during the gel precipitation stage (prior to the SHT treatment), but also during the crystallization process of the material was investigated. Syntheses were performed in the SHT reactor at 100 °C, varying the synthesis time from 15 minutes to 1 hour. Remarkably, the characteristic diffraction lines of zeolite A can be observed unequivocally on the XRD pattern after just 25 minutes of sonohydrothermal treatment at 100 °C. SEM analyses also confirm the sole occurrence of zeolite A under these conditions, pointing out a drastic kinetic increase under the joint action of 20 kHz ultrasound and hydrothermal conditions at 100 °C compared to the conventional HT treatment (Figure 1b). The sonofragmentation of the gel due to the local strong physical effects induced by cavitation bubbles resulted in a faster crystallization rate when the absorbed acoustic power in the reactor was varied. Zeolite A with smaller particles size were obtained as a result of an enhanced mass transfer induced by the acoustic cavitation phenomenon. Additionally, our study also highlighted the strong impact of the absorbed acoustic power on the conversion of zeolite A to sodalite and the underlying mechanism.



**Fig. 1.** Scheme of the sonohydrothermal reactor (a) and XRD patterns of the synthesized materials (b)

[1] Cau, C. & al. *J. Phys. Chem. C* **2013**, *117* (44), 22827–22833.



---

**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

## **One-Pot Synthesis of Zn-containing nanosized MFI zeolites**

**Diógenes Honorato Piva**, Sajjad Ghojavand, Francesco Dalena, Svetlana Mintova  
*Laboratoire Catalyse et Spectrochimie (LCS), Normandie Université, ENSICAEN, CNRS, 14000, Caen, France*

Embedding heteroatoms into zeolite frameworks is still a challenging and cutting-edge technology in the preparation of functional metal-containing zeolite catalysts.<sup>1</sup> Herein, nanosized Zn-MFI type zeolite with varying Zn content have been successfully prepared via one-pot synthesis strategy. The substitution of framework Si by Zn significantly reduces the silanol defect content. In addition, the insertion of Zn into the MFI structure induces a symmetry lowering, from orthorhombic (Pnma), typical of high silica MFI, to monoclinic (P2<sub>1</sub>/n). Quantitative FTIR spectroscopy with pyridine reveals the regeneration of Lewis acid sites. At a low Zn content (< 0.16 wt %) the concentration of Lewis sites remains constant, while the intensity of the bands corresponding to the Lewis acid sites increases almost linearly with the Zn loadings (< 0.6 wt %), and then levels off. In situ FTIR spectroscopy under reductive conditions revealed the evolution from isolated Zn<sup>2+</sup> cations to small (ZnO)<sub>n</sub> clusters in the MFI zeolite as the zinc content increases. The efficient strategy towards incorporation of various Zn species into the zeolite has been developed.

### **Références**

1. Julien Grand, Siddulu Naidu Talapaneni, Aurélie Vicent, Christian Fernandez, Eddy Dib, Hristiyan A. Aleksandrov, Georgi N. Vayssilov, Richard Retoux, Philippe Boullay, Jean-Pierre Gilson, Valentin Valtchev<sup>1</sup> and Svetlana Mintov, One-pot synthesis of silanol-free nanosized MFI zeolite *Nature Materials*, 16, 1010–1015 (2017).

**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

**CO<sub>2</sub> adsorption behaviour of nanosized CHA zeolites synthesised in the presence of barium or calcium cations**

**Aymeric Magisson**, Edwin B. Clatworthy,<sup>\*</sup> Sajjad Ghojavand, Philippe Bazin, Valérie Ruaux, Eddy Dib, Svetlana Mintova,<sup>\*</sup>

*Normandie Université, ENSICAEN, UNICAEN, CNRS, Laboratoire Catalyse et Spectrochimie (LCS), 14050 Caen, France*

Solid adsorbents such as zeolites are prime candidates for CO<sub>2</sub> capture and storage (CCS) applications. Small pore zeolites are microporous solids possessing an 8-membered ring aperture allowing guest molecules to enter in channels and cages in the presence of extra-framework cations. The use of alkaline-earth metal cations impacts not only the crystallisation kinetics of zeolites but also their adsorption behaviour [1].

Here we present the synthesis of nano-sized chabazite (CHA) zeolite samples using high charge-density alkaline earth metal cations (Ba<sup>2+</sup>, Ca<sup>2+</sup>) added to a precursor mixture containing alkali-metal cations (Na<sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup>). Partial substitution of the Na<sup>+</sup> and the pore-blocking Cs<sup>+</sup> extra-framework cations is observed for Ca-CHA that depends on the amount of K<sup>+</sup> used in the synthesis. While a change of the Na<sup>+</sup> amount is observed only for Ba-CHA zeolite. The type of alkaline-earth metal cations affects the crystallisation kinetics while keeping the same morphology of the crystals; slower crystallisation in the presence of Ca<sup>2+</sup> (10 h to full crystallinity) and similar crystallisation rate in the presence of Ba<sup>2+</sup> (4 h to full crystallinity) are observed. The nano-sized CHA zeolites were characterised by ICP-MS, SEM, XRD, DLS, TGA, N<sub>2</sub> and CO<sub>2</sub> physisorption, and <sup>27</sup>Al and <sup>29</sup>Si MAS NMR. As a reference material, nanosized CHA zeolite with crystals size of 200 nm and a Si/Al ratio of 2 was used [2].

The presence of Ca<sup>2+</sup> or Ba<sup>2+</sup> extra-framework cations leads to N<sub>2</sub> uptake values of 290 and 169 mmol g<sup>-1</sup> (-196 °C, 100 kPa), respectively, while at low CO<sub>2</sub> pressure (<1 kPa, 25 °C), the physisorbed CO<sub>2</sub> capacity for Ref-CHA, Ca-CHA, and Ba-CHA zeolites is 0.63, 0.66, and 0.59 mmol g<sup>-1</sup>, respectively. Interestingly, an opposite effect is observed for the amount of chemisorbed CO<sub>2</sub> species on the same samples.

**References**

- [1] A. Magisson, E. B. Clatworthy, S. Ghojavand, P. Bazin, V. Ruaux, E. Dib, and S. Mintova, *Advanced Sustainable Systems*, **2023**, 2300326 1–9.  
[2] M. Debost, P. B. Klar, N. Barrier, E. B. Clatworthy, J. Grand, F. Laine, P. Brázda, L. Palatinus, N. Nesterenko, P. Boullay, and S. Mintova, *Angew Chem.*, **2020**, vol. 59, 23491–23495.





**THEME**

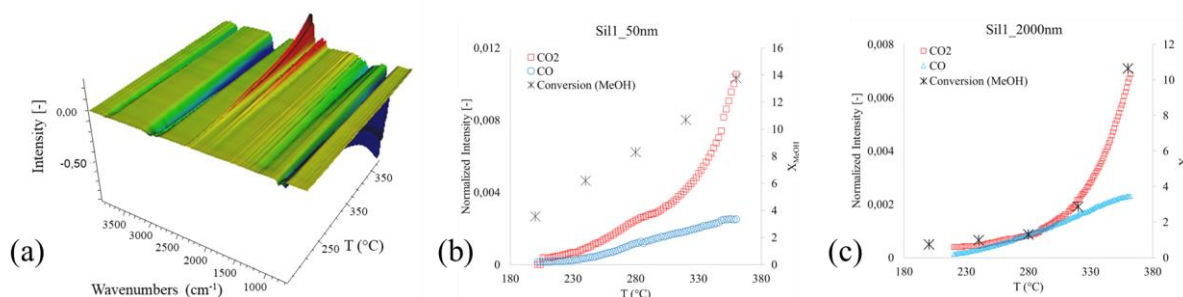
- Thème 1 : Elaboration et mise en forme de matériaux poreux  
 Thème 2 : Applications pour environnement, énergie et santé  
 Thème 3 : Modélisation et caractérisation de matériaux poreux

**Role of silanol defects in ZSM-5 zeolite in the methanol to hydrocarbons catalytic reaction**

**Francesco Dalena, Eddy Dib and Svetlana Mintova**

Normandie Univ, ENSICAEN, UNICAEN, CNRS, Laboratoire Catalyse et Spectrochimie, Caen, 14000, France

Zeolites are well-known catalysts for the conversion of methanol to hydrocarbons (MTH). By altering the synthesis procedure, the activity and the deactivation of zeolites in the conversion of methanol can be significantly altered. In fact, there is a strong dependence of the catalytic behavior in terms of conversion and deactivation speed not only related with the acidity of the zeolite catalyst, or the framework type structure or pore systems, but also with the silanol type defects [1]. However, the role of these silanol defects is not well known. To investigate how the catalytic activity is dependent on the number and type of defects, we performed the MTH reaction in the temperature range of 200-360 °C using two samples of Silicalite-1 with different particle sizes (2000 nm and 50 nm). The silanol sites of the two samples were first probed by adsorption of carbon monoxide (CO) and followed by in situ FT-IR spectroscopy. The analysis indicated that in both samples there are five different silanols species, but with different relative concentrations. The catalytic results, acquired with the operando IR system (WHSV: 1.77 g<sub>MeOH</sub> g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>) have shown the catalytic activity towards the formation of CO<sub>2</sub> and CO using both samples, but with different conversion and selectivity degrees. Specifically, the sample with particle size of 2000nm (Sil\_2000nm) tends to have a low net conversion (2.86) up to 320 °C, while the Sil1\_50nm sample appears to be much more active (10.69). At increased temperature (360 °C), the Sil1\_50nm sample has similar conversion (13.77), while Sil\_2000nm sample shows a clear increase of the conversion (10.64). The results clearly demonstrate the importance of various silanol defects (internal or external) on the catalytic activity of the catalysts. The data presented in this work clearly shows that the catalytic activity of internal defects plays an important role in the deactivation of the catalyst at higher temperature, while at lower temperatures the isolated external defects play an important role in the deactivation of the catalysts.



**Fig. 1.** FTIR operando methanol to hydrocarbons tests (WHSV: 1.77 g<sub>MeOH</sub> g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>) performed in the range 200-360 °C (a); Conversion and normalized intensity of the CO<sub>2</sub> and CO of Sil1\_50 nm (b) and Sil1\_2000nm (c) samples.

**Références**

[1] K. Barbera, F. Bonino, S. Bordiga, T.V. Janssens, P. Beato, J. Catal. 280(2) (2011) 196-205



## 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

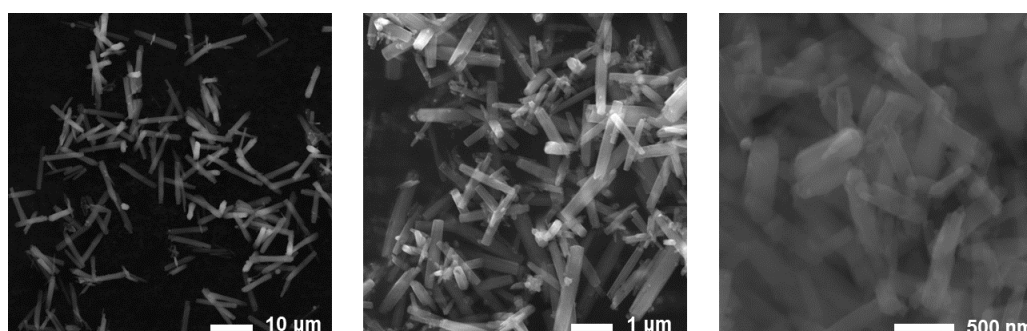
### OSDA-free synthesis of offretite for CO<sub>2</sub> adsorption

Risheng Wang,<sup>a</sup> Qiudi Yue,<sup>a</sup> Svetlana Mintova<sup>a\*</sup>

<sup>a</sup> Normandie Université, ENSICAEN, UNICAEN, CNRS, Laboratoire Catalyse et Spectrochimie (LCS), 14050 Caen, France

Solid adsorbents such as zeolites are promising candidate for CO<sub>2</sub> capture and storage applications. Currently, several small-pore zeolites (such as CHA and RHO) have been used in CO<sub>2</sub> adsorption[1]. Offretite is a zeolite consisting of channels (12-membered ring) and cages (8-membered ring opening).[2] Due to the tunable Si/Al ratio (2-5) and suitable size of the cages, offretite is expected to have a great potential in CO<sub>2</sub> capturing. However, the conventional micron-sized zeolites usually exhibit slow kinetics in CO<sub>2</sub> adsorption since the long diffusion path and slow diffusion kinetics within particles[3]. On the other hand, considering the economical cost and environmental problems, the utilization of organic templates (such as TMA and CTAB) should be reduced. Therefore, the use of OSDA-free strategy to obtain nano-sized offretite for CO<sub>2</sub> adsorption has to be considered.

Here, the OSDA-free synthesis of pure offretite using the mixed alkali metal cations (K<sup>+</sup>, Na<sup>+</sup> and Cs<sup>+</sup>) as inorganic SDAs in hydrothermal (HT) condition are presented. The synthetic parameters (cations content, Si/Al ratio) were optimized to get the pure phase. Further, to downsize the obtained micron crystals, the aging time, HT temperature and HT time were varied. The obtained offretite zeolites were characterized by XRD, SEM, ICP-MS, TGA and CO<sub>2</sub> physisorption. It was revealed that longer aging time accelerates the crystallization kinetics and leads to a shorter HT time and a lower essential HT temperature. Microscopic analysis showed that by tuning the crystallization temperature and aging time synergistically, the sizes of crystals were efficiently downsized from 20 μm to 500 nm. CO<sub>2</sub> physisorption isotherms revealed that the obtained offretites have good capacities for CO<sub>2</sub> at 298 K. All the results show that OSDA-free strategy is a promising way to obtain the offretite with high quality for CO<sub>2</sub> adsorption.



**Fig. 1** SEM images of samples synthesized at different conditions: aging for 7 days followed by a HT crystallization at 130°C (a); aging for 21 days followed by a HT crystallization at 90°C (b); aging for 21 days followed by a HT crystallization at 60°C (c).

## Références

- [1] Boer, D. G.; Langerak, J.; Pescarmona, P. P. *ACS Appl. Energy Mater.* **2023**, *6*, 2634–2656.  
 [2] Patuwan, S.Z.; Arshad, S.E. *Materials*, **2021**, *14*, 2890.  
 [3] Clatworthy, E. B.; Ghojavand, S.; Guillet-Nicolas, R.; Gilson, J. P.; Llewellyn, P. L.; Nesterenko, N.; Mintova, S. *Chem. Eng. J.* **2023**, *471*, 144557.



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

## THÈME

Thème 2 : Applications pour environnement, énergie et santé

Thème 3 : Modélisation et caractérisation de matériaux poreux

## Synthesis and characterization of manganese-containing nanosized MFI zeolite

Marco Geloso<sup>1</sup>, Sajjad Ghohavand<sup>1\*</sup>, Edwin Clathworthy<sup>1</sup>, Francesco Dalena<sup>1</sup>, Glorija Medak<sup>1</sup>, Aymeric Magisson<sup>1</sup>, Valerie Ruaux<sup>1</sup>, Rossella Arletti<sup>2</sup>, Riccardo Fantini<sup>2</sup>, Diogenes Honorato Piva<sup>1</sup>, Svetlana Mintova<sup>1\*</sup>

<sup>1</sup>Normandie Université, ENSICAEN, UNICAEN, CNRS, Laboratoire Catalyse et Spectrochimie (LCS), 14000 Caen, France

<sup>2</sup>Università di Modena, Dipartimento di Scienze chimiche e biologiche, 41125 Modena, Italy

Zeolites are crystalline microporous aluminosilicate materials employed in various applications due to their high thermal stability, catalytic activity and selectivity. By minimizing the size of zeolites, reagents encounter a shorter diffusion path to reach an active site, thus facilitating the conversion into products.<sup>1</sup> Catalytic deactivation primarily results from coke production within the zeolite structure, a phenomenon directly associated with interactions with silanol groups ( $\equiv\text{Si}-\text{OH}$ ). To mitigate this issue, the reduction of silanol groups is needed, requiring the utilization of various direct and post synthesis treatments.<sup>2</sup>

An approach to synthesize nanosized silanol-free zeolites with enhanced catalytic performance involves the incorporation of highly active transitional metals into the zeolite framework. A synergy between the zeolite features and of atomic-guest species resulting in improved catalysts has been reported.<sup>3,4</sup>

$\text{Mn}_x\text{O}_y$  nanoparticles and manganese-containing compounds have been reported as promising catalysts for degradation of organic pollutants and biodiesel production<sup>5</sup>. However, these materials suffer from low thermal stability (ex. at 535 °C for  $\text{MnO}_2$ ).<sup>6</sup> In contrast, zeolites have shown exceptional thermal stability controlled by variation of silanol defects (stable at more than 700 °C).<sup>4,6</sup>

In this study, the green synthesis of nanosized silanol-free manganese-containing MFI zeolite is reported. Based on our previous work on metal-containing zeolites<sup>4</sup>, potassium permanganate ( $\text{KMnO}_4$ ) was added as silanol preventing agent in the initial precursor suspensions. The hydrothermal synthesis of Mn-containing zeolite was carried out at 90°C for 48 h. The size of the crystals and chemical composition were determined by FESEM.

Based on Rietveld refinement, the space group for Mn-containing zeolites (Mn-MFI) and the reference sample (Si-MFI) as  $P2_1/n$  and  $Pnma$ , respectively were determined. This observation is similar to our previous findings on tungsten and molybdenum containing zeolites.<sup>4,7</sup>

<sup>29</sup>Si MAS NMR spectroscopy showed no evidence of Q<sup>3</sup> species (silanol groups) in the Mn-MFI zeolite. ICP-MS and SEM/EDX revealed the Mn amount of ~0.2 at. % in the MFI crystals. Finally, the high stability of the Mn-MFI zeolite was confirmed by in situ PXRD. The Mn-MFI nanosized zeolite will be considered for catalytic degradation of organic pollutants or bio diesel production especially when high temperature is needed.

## Références

- (1) Mintova, S.; Grand, J.; Valtchev, V. Nanosized Zeolites: Quo Vadis? *Emerg. Chem. Fr.* **2016**, *19* (1), 183–191. <https://doi.org/10.1016/j.crci.2015.11.005>.
- (2) Qin, Z.; Lakiss, L.; Tosheva, L.; Gilson, J.-P.; Vicente, A.; Fernandez, C.; Valtchev, V. Comparative Study of Nano-ZSM-5 Catalysts Synthesized in OH<sup>-</sup> and F<sup>-</sup> Media. *Adv. Funct. Mater.* **2014**, *24* (2), 257–264. <https://doi.org/10.1002/adfm.201301541>.
- (3) Medeiros-Costa, I. C.; Dib, E.; Nesterenko, N.; Dath, J.-P.; Gilson, J.-P.; Mintova, S. Silanol Defect Engineering and Healing in Zeolites: Opportunities to Fine-Tune Their Properties and Performances. *Chem. Soc. Rev.* **2021**, *50* (19), 11156–11179. <https://doi.org/10.1039/D1CS00395J>.
- (4) Grand, J.; Talapaneni, S. N.; Vicente, A.; Fernandez, C.; Dib, E.; Aleksandrov, H. A.; Vayssilov, G. N.; Retoux, R.; Boullay, P.; Gilson, J.-P.; Valtchev, V.; Mintova, S. One-Pot Synthesis of Silanol-Free Nanosized MFI Zeolite. *Nat. Mater.* **2017**, *16* (10), 1010–1015. <https://doi.org/10.1038/nmat4941>.
- (5) Dias, J. M.; Alvim-Ferraz, M. C. M.; Almeida, M. F.; Méndez Díaz, J. D.; Sánchez Polo, M.; Rivera Utrilla, J. Biodiesel Production Using Calcium Manganese Oxide as Catalyst and Different Raw Materials. *Energy Convers. Manag.* **2013**, *65*, 647–653. <https://doi.org/10.1016/j.enconman.2012.09.016>.
- (6) Wang, L.; Wang, L.; Meng, X.; Xiao, F.-S. New Strategies for the Preparation of Sinter-Resistant Metal-Nanoparticle-Based Catalysts. *Adv. Mater.* **2019**, *31* (50), 1901905. <https://doi.org/10.1002/adma.201901905>.
- (7) Dubray, F.; Moldovan, S.; Kouvatias, C.; Grand, J.; Aquino, C.; Barrier, N.; Gilson, J.-P.; Nesterenko, N.; Minoux, D.; Mintova, S. Direct Evidence for Single Molybdenum Atoms Incorporated in the Framework of MFI Zeolite Nanocrystals. *J. Am. Chem. Soc.* **2019**, *141* (22), 8689–8693. <https://doi.org/10.1021/jacs.9b02589>.

**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

**Study of the hydrophobicity of Al-SBA-15 mesoporous materials****Z. Talha<sup>a</sup>, R. Hamacha<sup>a</sup>, C. Bachir<sup>b</sup>, F. Villières<sup>c</sup>, A. Bengueddach<sup>a</sup>**<sup>a</sup> *Laboratory of Chemistry Materials L.C.M., University of Oran 1 Ahmed Ben Bella, Algérie.*<sup>b</sup> *Laboratory of Chemistry Applied LAC, C.U. Aïn-Témouchent, Algérie.*<sup>c</sup> *Inerdisciplinary Laboratory of Continental Environments LIEC, UMR 7360 CNRS – University of Lorraine, Nancy, France.*

In 1998, a prominent research which produces hexagonal array and uniform mesoporous channel namely SBA-15 (Santa Barbara Amorphous N<sup>o</sup> 15) by Zhao et al [1]. These mesoporous silica are highly ordered, large specific surface area (up to 1000 m<sup>2</sup>/g), larger pore size (4.6–30 nm) and thicker pore walls (3.1–6.4 nm) [1-2] with thicker pore which give the material good hydrothermal stability unlike the M41S family because of the presence of silanol groups in the latter, Si-OH surface silanols have a hydrophilic character thanks to the possibility of forming hydrogen bonds with water molecules. Since SBA-15 does not have many silanol groups, it mainly presents Si-O-Si siloxane bridges which have a hydrophobic character [3-6].

In this study was interested in the functionalization of SBA-15 mesoporous materials by the incorporation of aluminum for different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios and to see the effect of hydrophobicity. The obtained solids were characterized using powder X-ray diffraction (XRD), N<sub>2</sub> adsorption-desorption, transmission electron microscopy (TEM) and water adsorption. This last analysis also made it possible to estimate the hydrothermal stability and hydrophobicity of these materials.

The results show that the adsorption isotherms are of type V, in the IUPAC classification, suggesting a weak interaction between water vapor and the hydrophobic surface of the SBA-15 surface [4]. The changes in hydrophobic properties and surface charge show that aluminium is incorporated into the SBA-15 framework and is related to lower silanol groups concentration after Al post synthesis.

**References**

- [1] Zhao D, Huo Q, Feng J, Chmelka BF, Stucky GD (1998) *J Am Chem Soc* 120:6024–6036  
[2] Li Q, Wu Z, Tu B, Park SS, Ha CS, Zhao D (2010) *Microporous Mesoporous Mater* 135:95–104  
[3] Anderson M, Klinowski XJ (1986) *J Chem Soc Faraday Trans* 82:1449  
[4] Pires J, Pinto M, Estella J, Echeverria JC JC (2008) *J Colloid Interface Sci* 317:206–213  
[5] Zhang K, Lively RP, Noel JD, Dose ME, Cool BAM, Chance RR, Koros WJ (2012) *Langmuir* 28:8664–8673  
[6] Zhao G, Zhao Z, Wu J, Ye D (2014) *J Spectroscopy* 2014:7 (Article ID 965037)

**THEME**

- Thème 1 : Elaboration et mise en forme de matériaux poreux  
 Thème 2 : Applications des matériaux poreux  
 Thème 3 : Modélisation et caractérisation de matériaux poreux

**Coupled plasmon modes with molecule-like clusters confined in ZX zeolite: Photoassisted electrochemical preparation and characterization**

Mama **Lafjah**<sup>a</sup>, Mohamad **El-Roz**<sup>b</sup>, Fatiha **Djafri**<sup>b</sup>, Fatima **Douma**<sup>a,b</sup>

<sup>a</sup> *Université Ahmed ben Bella (Laboratoire de chimie des matériaux Oran1, Oran, Algérie)*

<sup>b</sup> *Normandie Université ( ENSICAEN, UNICAEN, CNRS, Laboratoire Catalyse et Spectrochimie, 14050 Caen, France)*

Like-molecule silver cluster have been reported to show a unique electro-optical behavior resulting from the discrete energy transitions and the strong fluorescence. Silver clusters have widely employed in different fields like: imaging, sensing, optoelectronic, catalytic and extended to photocatalytic applications. In this work Bismuth ( $\text{Bi}^{2+}/\text{Bi}^{3+}$ )-doped zeolite nanoparticles (ZX-Bi), successfully prepared using one-pot hydrothermal synthesis and stabilized as colloidal suspensions, were used for the preparation of bridged silver clusters. UV-irradiation of the ZX-Bi suspensions in the presence of silver nitrate promotes the formation of reduced silver particles ( $\text{Ag}@ZX\text{-Bi}$ ) in the zeolite micropore space. The set of experimental results revealed that the optical behavior of the confined silver particles depends on the Bi concentration initially introduced into the zeolite. The composite sample's UV-visible absorbance shows narrow bands in the visible range (400–800 nm), which is characteristic of metal nanoparticles with well-defined sizes. The TEM analysis, the photoluminescence results, and the boundary element method (BEM) approach showed that the unique optical behavior of Ag is a consequence of the formation of interconnected silver clusters (silver quasi-nanoparticles) through the zeolite channels. The IR operando analysis of the samples in the dark and under visible-light irradiation confirmed the surprising plasmonic behavior of the  $\text{Ag}@ZX\text{-Bi}$  samples and registered local heating equivalent to 190 °C under visible irradiation, behavior that is characteristic of plasmonic nanoparticles. Therefore, to our knowledge, the gap between clusters and plasmonic nanoparticles with the well-controlled and reproducible size of Ag-QNPs is bridged for the first time. The simplicity of the used method allows easy scale-up for different possible applications ( $\mu$ -sensors, electronics, optics, etc.).[1,2]



---

[1] M. El-Roz, I. Telegeiev, N. E. Mordvinova, O.I. Lebedev, N. Barrier, A. Behlil, M. Zaarour, L. Lakiss, V. Valtchev, *ACS Appl Mater Interfaces*. **10** (2018) 28702-28708

[2] F. Douma, L. Lakiss, O. I. Lebedev, J. Cardin, K. L. Kostov, J. El Fallah, ... & M. El-Roz,. Silver quasi-nanoparticles: bridging the gap between molecule-like clusters and plasmonic nanoparticles. *Materials Advances*, **2**(2021), 5453-5464.

**THÈME**

- 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

**One-pot synthesis of hierarchical Y/ nano-ZSM-5 composite zeolite for fluid catalytic cracking**

Ruizhe Zhang,<sup>a</sup> Yanfeng Shen,<sup>a</sup> Jiani Xu,<sup>a</sup> Bo Wang,<sup>a</sup> Hongjuan Zhao,<sup>b</sup> Shutao Xu,<sup>c</sup> Zifeng Yan,<sup>a</sup>  
Zhengxing Qin,<sup>a,\*</sup> Svetlana Mintova<sup>a,d\*</sup>

<sup>a</sup> *State Key Laboratory of Heavy Oil Processing, College of Chemical Engineering, China University of Petroleum (East China), No. 66, West Changjiang Road, Huangdao District, Qingdao, China, 266580.*

<sup>b</sup> *Petrochemical Research Institute, PetroChina Company Limited, Beijing 100195, P. R. China*

<sup>c</sup> *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China.*

<sup>d</sup> *Laboratoire Catalyse et Spectrochimie, Normandie Univ, ENSICAEN, UNICAEN, CNRS, 6 Bd Marchal Juin, Caen, France, 14000.*

The fluid catalytic cracking (FCC) process is one of the most important oil refinery processes due to its capability of converting low-valuable feedstocks into highly demanded products, including gasoline, diesel, and light olefins, particularly propylene and butene. In order to enhance the yield for C<sub>3</sub>-C<sub>4</sub> olefins, the ZSM-5 zeolite was used as one of the main component of the FCC catalysts.[1] Currently, the most common approach for the incorporation of the ZSM-5 is through the mechanical mixing of all active components together with a binder followed by spray granulation.

In the present work, we report a new strategy for preparation of hierarchical composite consisting of both zeolite Y and nanosized ZSM-5 zeolites in one-pot via partial inter-zeolite transformation[2]. The experimental conditions were optimized for the preparation of hierarchical composites with different FAU to MFI ratios. The synthesized composites were studied in detail using a set of comprehensive physical and chemical characterization methods. The composite samples showed substantially improved catalytic performance in the cracking of crude oil.

**Acknowledgements**

We acknowledge the financial support from the National Natural Science Foundation of China (22178389) and PetroChina (KYWX-21-021, PRIKY21084).

**Références**

- [1] Degnan T F, Chitnis G K, Schipper P H. History of ZSM-5 fluid catalytic cracking additive development at Mobil[J]. *Microporous and Mesoporous materials*, 2000, 35: 245-252.  
[2] Zhengxing Qin, Yanfeng Shen, Xinmei Liu, et al. A method for the preparation of composite zeolites. [P]. 2020, CN109437230B.



**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

**Synthesis of SAPO-34 molecular sieves with adjustable defect sizes using industrial waste catalysts**

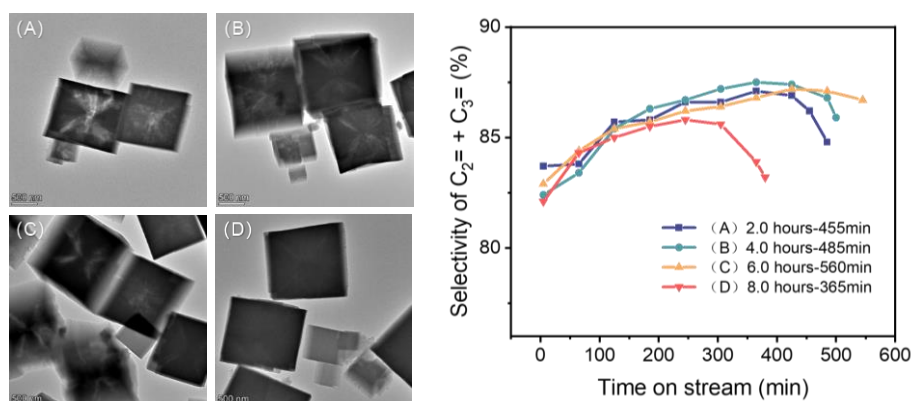
Yue. Hu,<sup>a,b</sup> Xin Mei Liu<sup>a,b</sup>, Yu Chao Lyu<sup>a,b</sup> Mathias Barreau,<sup>a</sup> Svetlana Mintova<sup>a,\*</sup>

<sup>a</sup> Laboratoire Catalyse et Spectrochimie (LCS), CNRS, 14050 Caen, France.

<sup>b</sup> State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Qingdao, 266580, China

SAPO-34 zeolite was synthesized using waste catalysts from Methanol to Olefins (MTO) process as a source of Al, Si and P. SAPO-34 samples with high crystallinity for short crystallization time were obtained. The presence of fragments containing characteristic secondary building blocks (SBUs) of the SAPO-34 material in the gel facilitated the crystallization process but also let to the formation of defect-enriched structures following the dissolution-recrystallization mechanism.

In this work, waste MTO catalysts first was subjected to phosphoric acid treatment leading to the formation of small fragments with abundant secondary building blocks. Then they were treated with an organic agent. The size and concentration of defects in the zeolite crystals were varied by prolonging the phosphoric-acid pretreatment time. The SAPO-34 samples with defects of different sizes showed significant differences in the catalytic performance in the MTO reaction (**Figure 1**).



**Fig. 1.** The TEM images and MTO catalytic test results of samples synthesized using waste catalysts subjected to different time of phosphoric acid pretreatment: (A) 2.0 hours, (B) 4.0 hours, (C) 6.0 hours and (D) 8.0 hours



# POSTERS

## THEME 2



**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

**Metal-Organic Frameworks: Evaluating cytotoxicity assays and their antiviral activity against coronaviruses**

Orfeas-Evangelos Plastiras,<sup>a,b</sup> Peggy Bouquet,<sup>c</sup> Jeremy Dhainaut,<sup>a</sup> Jean-Philippe Dacquin,<sup>a</sup> Anne Goffard<sup>b</sup> and Christophe Volkringer<sup>a</sup>

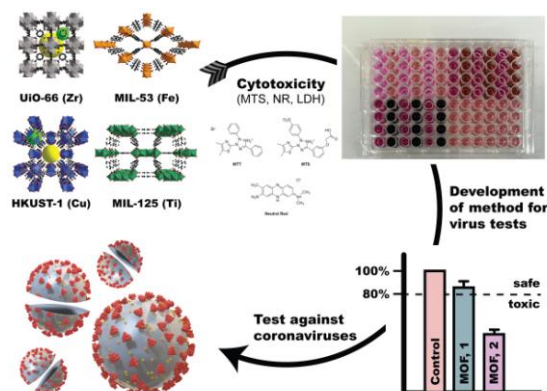
<sup>a</sup> UMR CNRS 8181, Unité de Catalyse et Chimie du Solide, Centrale Lille, CNRS, Université de Lille, 59000 Lille, France.

<sup>b</sup> U1019 – UMR 9017 – CIIL - Center for Infection and Immunity of Lille, Institut Pasteur de Lille, Université de Lille, CNRS, INSERM, CHU de Lille, 59000 Lille, France.

<sup>c</sup> Clinical Microbiology Unit, Institut Pasteur de Lille, Lille F-59000, France

Severe acute respiratory syndrome coronavirus-2 (SARS-CoV-2) is responsible for the corona virus disease of 2019, or else COVID-19, which originated from Wuhan of China in December of 2019.<sup>[1]</sup> Up to this day, this disease that was declared a pandemic by WHO on March 11 of 2020 is accountable for 6.8 million deaths and 758 million cases worldwide as of March 6<sup>th</sup> 2023.<sup>[2]</sup>

In this work, metal-organic frameworks synthesized with different metals (Zr, Cu, Fe, Ti) were used to evaluate different cytotoxicity methods in three cell lines, named MTS, Neutral Red and LDH as cytotoxicity methods and Huh7 Tmprss2, VeroE6 and Vero81 as cell lines. Different concentrations were tested and the Neutral Red method was found to be the most precise and accurate, Furthermore, their antiviral effect against coronaviruses (e.g. SARS-CoV-2) was examined with different tests, that were able to determine both the viral titer and the infectivity of the virus.<sup>[3]</sup>



**Fig. 1:** Representative graphical scheme of the protocol used for the inactivation of coronaviruses.

**Références**

[1] Zheng, J., *Int. J. Biol. Sci.*, **2020**, 16 (10), 1678-1685.

[2] <https://www.who.int/emergencies/diseases/novel-coronavirus-2019> (Accessed on March 6<sup>th</sup> 2023)

[3] Plastiras, O.-E., Bouquet, P., Loiseau, T., Goffard, A., Volkringer, C. Metal-Organic Frameworks: Evaluating cytotoxicity assays and their effectiveness against SARS-CoV-2 (submitted).



THÈME

- 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

## Unconventional coke composition originating from anisole disproportionation on zeolites

N. Pichot<sup>a,b,c</sup>, N. Chaouati<sup>c</sup>, Y. Pouilloux<sup>a</sup>, A. Dufour<sup>b</sup>, L. Pinard<sup>c</sup>

<sup>a</sup> IC2MP, UMR 7285, Poitiers

<sup>b</sup> LRGP, UMR 7274, Nancy

<sup>c</sup> LCS, UMR 6506, Caen

Anisole disproportionation is a model reaction for the study of catalytic fast pyrolysis of lignocellulosic biomass, for the production of high value aromatic hydrocarbons (benzene, toluene, xylenes). The major hurdle to commercialisation of this process is the catalyst deactivation. Previous work on anisole disproportionation on MFI zeolites showed a steady-state activity was achieved after a short time, and that it was caused by the nature of the deactivating species, being methylated phenolics, i.e. the main reaction products:  $(CH_3)_x$ -Phenol, with  $0 < x < 4$  [1]. No polyaromatics were found after extraction of the coke species, which was ascribed to the steric hindrance of the 10-MR channels in MFI.

In the present study, anisole disproportionation was carried out on 12-MR zeolites in addition to the previous MFI. Again, no polyaromatic coke was found after extraction, instead the previously mentioned methylphenols were found, with higher selectivities than previously for the pentamethylphenol, due to the lower steric constraints in the 12-MR zeolites (Figure 1a). The unusual absence of polyaromatic species in the coke extract can be explained by the inhibition of the paring mechanism[2], usually found in hydrocarbon transformation processes, by the electronic effects induced by the hydroxyl group of the phenolics (Figure 1b).

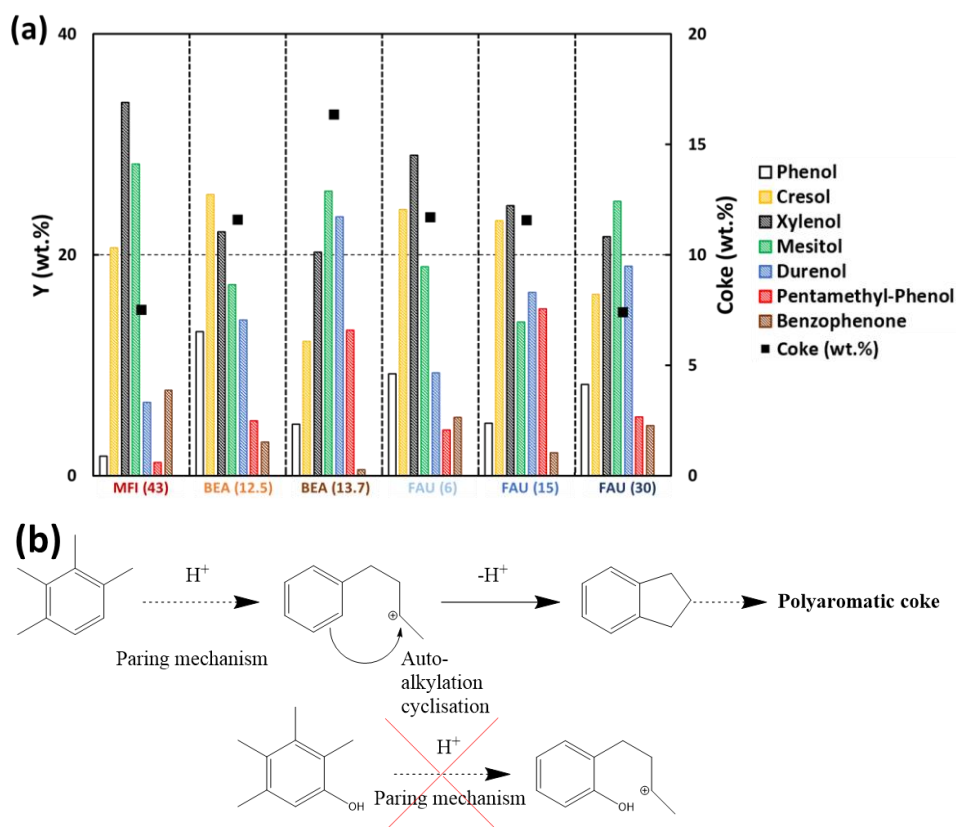


Figure 1: (a) Main coke components on different zeolite structures and acidities; (b) Inhibition of the paring mechanism by the hydroxyl group

Références

[1] N. Pichot, J.W. Hounfodji, et al. Appl. Catal. A, **665**, (2023)

[2] L. Pinard, S. Hamieh et al. J. Catal., **299**, 284-297, (2013)



Thème 1 : Elaboration et mise en forme de matériaux poreux

## THÈME

Thème 2 : Applications pour environnement, énergie et santé

Thème 3 : Modélisation et caractérisation de matériaux poreux

### Enhancing the efficiency of CO<sub>2</sub> removal by reducing the size of zeolite crystals

Sajjad Ghojavand<sup>a</sup>, Edwin Clatworthy<sup>a</sup>, Rémy Guillet-Nicolas<sup>a</sup>, Benoit Coasne<sup>b</sup>, Veronique Pugnet<sup>c</sup>,

Parveen Kumar-Gandhi<sup>c</sup>, Svetlana Mintova<sup>a</sup>

<sup>a</sup>Normandie Université, ENSICAEN, UNICAEN, CNRS, Laboratoire Catalyse et Spectrochimie (LCS), 14000 Caen, France

<sup>b</sup>Université Grenoble Alpes, CNRS, Laboratoire Interdisciplinaire de Physique (LIPhy), 38000 Grenoble, France

<sup>c</sup>TotalEnergies, OneTech, Sustainability R&D, CSTJF, 64018 Pau Cedex, France

sajjad.ghojavand@ensicaen.fr

Due to the rising atmospheric concentration of CO<sub>2</sub> from human activities, the separation of CO<sub>2</sub> from N<sub>2</sub>, commonly referred to as flue gas, has become a crucial priority.[1] There are four prevalent technologies used for CO<sub>2</sub> capture: (i) adsorption with amine-based solvents, (ii) adsorption by nanoporous solids, (iii) cryogenic distillation, and (iv) membrane separation. Zeolites, among the materials considered for CO<sub>2</sub> adsorption, offer the advantage of being inorganic, non-toxic substances with high thermal stability and selectivity, which can be adjusted by their framework structure and chemical composition.[1] Moreover, recent findings indicate that zeolites exhibit flexible structures.[2] This flexibility in zeolites is observable as a response to the adsorption or desorption of guest molecules. It can manifest as changes in the zeolite lattice parameters (framework dynamics) or by the relocation of extra-framework cations within zeolite pores (extra-framework dynamics).[1,2] Traditional zeolites face diffusion limitations of guest molecules through their pore networks due to their typical existence as micron-sized polycrystalline powders.[3] To overcome these limitations, various methods have been developed to increase the surface area/volume ratio. Among these approaches, nanozeolites consisting of discrete nanoparticles that result in a greater external surface area and a higher number of available active sites.[3]

We have successfully demonstrated the outstanding CO<sub>2</sub> capture capabilities of nanosized chabazite (CHA) zeolites in various alkali forms (Na<sup>+</sup>, K<sup>+</sup>, and Cs<sup>+</sup>).[1,3,4] In this study, we initially estimated CO<sub>2</sub> and N<sub>2</sub> equilibrium adsorption isotherms through Grand Canonical Monte Carlo (GCMC) calculations at 298 K. Subsequently, utilizing molecular dynamics simulations, we determined the self-diffusivities of CO<sub>2</sub> molecules at different loadings for various CHA nanocrystals. The experimental validation of dynamic CO<sub>2</sub>/N<sub>2</sub> separation was conducted through breakthrough measurements, simulating a 17/83 (CO<sub>2</sub>/N<sub>2</sub>) mixed-component gas mixture package at 298 K (molar basis).

Based on the breakthrough measurement, we achieved dynamic saturation loadings of CO<sub>2</sub> 2.48, 1.72, and 0.57 mmol g<sup>-1</sup> for Na-CHA, K-CHA, and Cs-CHA nanosized zeolites, respectively, with CO<sub>2</sub>/N<sub>2</sub> molar selectivity at saturation measuring 62, 46, and 23. When comparing the nanosized (60 nm) Cs-CHA zeolite with its micron-sized (3 μm) counterpart, we observed notably faster CO<sub>2</sub> breakthrough kinetics for the nanosized Cs-CHA zeolite. Ultimately, this accelerated kinetic behavior resulted in a remarkable over 150% improvement in dynamic CO<sub>2</sub> removal.

In summary, different alkali forms of nanosized CHA zeolites prove to be exceptional materials for effectively separating CO<sub>2</sub> from N<sub>2</sub>.

**Acknowledgments:** The support of the Centre for Zeolites and Nanoporous Materials, Label of Excellence, Normandy Region (CLEAR). IRN Zeolites and TotalEnergies is acknowledged.

### References

- [1] S. Ghojavand, B. Coasne, E.B. Clatworthy, R. Guillet-Nicolas, P. Bazin, M. Desmurs, L. Jacobo Aguilera, V. Ruaux, S. Mintova, Alkali Metal Cations Influence the CO<sub>2</sub> Adsorption Capacity of Nanosized Chabazite: Modeling vs Experiment, *ACS Appl. Nano Mater.* 5 (2022) 5578–5588. <https://doi.org/10.1021/acsanm.2c00537>.
- [2] S. Ghojavand, E. Dib, S. Mintova, Flexibility in zeolites: origin, limits, and evaluation, *Chem. Sci.* (2023). <https://doi.org/10.1039/D3SC03934J>.
- [3] S. Ghojavand, E.B. Clatworthy, A. Vicente, E. Dib, V. Ruaux, M. Debost, J. El Fallah, S. Mintova, The role of mixed alkali metal cations on the formation of nanosized CHA zeolite from colloidal precursor suspension, *J. Colloid Interface Sci.* 604 (2021) 350–357. <https://doi.org/10.1016/j.jcis.2021.06.176>.
- [4] S. Ghojavand, E. Dib, J. Rey, A. Daouli, E.B. Clatworthy, P. Bazin, V. Ruaux, M. Badawi, S. Mintova, Interplay between alkali-metal cations and silanol sites in nanosized CHA zeolite and implications for CO<sub>2</sub> adsorption, *Commun. Chem.* 6 (2023) 1–8. <https://doi.org/10.1038/s42004-023-00918-1>.

**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

**Zéolithes modifiées par les nanoparticules de Fe et de Ni comme catalyseurs efficaces pour la réduction catalytique de polluants organiques**

**A. Mekki**<sup>a,b</sup>, **R. Hamacha**<sup>a,\*</sup>, **Adel Mokhtar**<sup>a,c</sup>, **M. Hachemaoui**<sup>a,d</sup>, **H. Habib Zahmani**<sup>f</sup>, **S. Hacini**<sup>f</sup>, **B. Boukoussa**<sup>a,b</sup>.

<sup>a</sup> *Laboratoire de Chimie des Matériaux L.C.M, Université Oran1 Ahmed Ben Bella, BP 1524, El-Mnaouer, 31000 Oran, Algeria*

<sup>b</sup> *Ecole Supérieure en Sciences Biologiques d'Oran (ESSBO), Emir Abdelkader Estate (EX-INESSMO), P.O. Box 1042, Saim Mohamed, Oran, 31000, Algeria*

<sup>c</sup> *Département Génie des Procédés, Institut des Sciences et Technologies, Université Ahmed Zabana, 48000 Relizane, Algeria*

<sup>d</sup> *Département de Sciences de la Matière, Institut des Sciences et Technologies, Université Ahmed Zabana, 48000 Relizane, Algeria*

<sup>e</sup> *Laboratoire de Chimie Fine LCF, Université Oran1 Ahmed Ben Bella, BP- 1524, El- Mnaouer, 31000 Oran, Algeria*

<sup>f</sup> *Département de Génie des Matériaux, Faculté de Chimie, Université des Sciences et de la Technologie Mohamed Boudiaf, BP 1505, El-Mnaouer, 31000 Oran, Algeria*

Auteur correspondant : rachidahamacha@gmail.com

**Résumé:**

Trois zéolithes de structures différentes (mazzite, faujasite et MFI) ont été préparées par voie hydrothermale, puis ont été utilisées pour stabiliser des nanoparticules de Fe et Ni par échange d'ions suivi d'un traitement avec une solution de NaBH<sub>4</sub> comme agent réducteur. Les nanocatalyseurs préparés ont été utilisés dans la réduction catalytique du colorant bleu de méthylène (BM) et du 4-nitrophénol (4-NP) dans un système simple et binaire sous une solution NaBH<sub>4</sub> afin de déterminer leur efficacité dans le traitement des eaux usées. Les échantillons obtenus ont été caractérisés par DRX, XPS, sorption d'azote à 77 K, XRF, IRTF, UV-vis, MEB et MET. Les résultats obtenus ont révélé que la structure des zéolithes demeure bien conservée après immobilisation de nanoparticules métalliques (NPs), mais leurs propriétés texturales sont légèrement réduites. Les résultats XPS montrent clairement que les nanoparticules à charge nulle ont été bien obtenues en utilisant une solution de NaBH<sub>4</sub>. Comme le confirme l'analyse MET, les nanoparticules sont bien dispersées à la surface des zéolithes et leurs tailles sont d'environ 3 à 13 nm pour les zéolithes modifiées par des FeNPs et de 2 à 6 nm pour celles modifiées par des NiNPs. Le catalyseur Ni-Y a présenté une excellente activité catalytique envers la réduction du colorant BM et du 4-NP dans un système binaire et simple en raison de sa grande surface contenant des nanoparticules de Ni bien dispersées. La constante de vitesse calculée dans le système simple est de 0,02 s<sup>-1</sup> et 0,005 s<sup>-1</sup> pour 4-NP et BM respectivement, alors que dans le système binaire, la constante est de 0,002 s<sup>-1</sup> et 0,014 s<sup>-1</sup>. Le catalyseur Ni-Y a été utilisé dans cinq expériences consécutives sans perte d'activité importante, confirmant sa stabilité.

Mots clés : Zéolithes, Zéolithes chargées de métaux, Réduction catalytique.



## 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

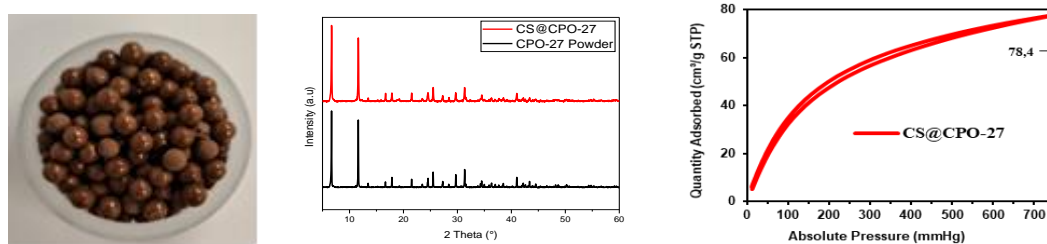
### Shaped MOF composites: promising materials in CCUS technology

Y. Khadiri<sup>a,b</sup>, A. Anouar<sup>b</sup>, S. Royer<sup>a</sup>, A. El Kadib<sup>b</sup>, T. Loiseau<sup>a</sup>, J. Dhainaut<sup>a</sup>

<sup>a</sup> UCCS – Unité de Catalyse et Chimie du Solide (UMR 8181), F-59000 Lille, France.

<sup>b</sup> Euromed Research Center, Engineering Division, Euro-Med University of Fes (UEMF),  
Route de Meknes, Rond-point de Bensouda, 30070 Fès, Morocco.

Metal–Organic Frameworks (MOFs) are highly porous and crystalline materials that emerged in the 2000s, and that have attracted great attention of researchers in different fields such as catalysis, energy storage and gas sorption. However, they have not yet reached the flowering stage in various applications on industrial scale due to their difficult processing and their low chemical and thermal stability. The combination of MOFs with polysaccharide is one of the strategies that have been developed recently to overcome MOFs' limitations, and to prepare composite materials with different shapes like monoliths, films, or microspheres [1]. Recently, we developed a novel approach based on the *in-situ* growth of MOFs within chitosan beads to obtain composites with superior adsorption properties [2]. Herein, this strategy has been further improved to prepare MOF-based composites with high CO<sub>2</sub> uptake capacity at room temperature. Especially, we achieved the preparation of CPO-27-based MOFs (see Figure 1), which are among the leading candidates for CO<sub>2</sub> capture, for the first time with this *in-situ* strategy.



**Fig. 1.** CS@CPO-27 microspheres (left), related XRD (middle) and CO<sub>2</sub> sorption isotherm – 298 K (right).

The prepared materials were used for CO<sub>2</sub> adsorption where they showed promising performances (2.6 mmol/g and 3.1 mmol/g at 298 K - 1 bar for CS@HKUST-1 and CS@CPO-27, respectively). This is the first time that such composite shows CO<sub>2</sub> sorption performance exceeding the performance of liquid amines (~ 2 mmol/g at 298 K - 1 bar).

## Références

- [1] Herbert Musarurwa, *et al.* Carbohydrate Polymers 275 (2022): 118743  
 [2] Nisrine Hammi, *et al.* ACS Applied Materials & Interfaces 15 (2023): 53395

**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

**Etude de l'adsorption en phase gaz dynamique et thermodésorption du 1,2 dichlorobenzène sur des faujasites 13X échangées au néodyme Nd<sup>3+</sup>**

Véronique WERNERT<sup>a</sup>, Angélique SIMON-MASSERON<sup>b,c</sup>, Laurence TORTET<sup>a</sup>, Aurika JANULYTE<sup>d</sup> and Yves ZEREGA<sup>a</sup>

<sup>a</sup> Aix-Marseille Université, CNRS, MADIREL, UMR 7246, Centre de Saint Jérôme, 13013 Marseille

<sup>b</sup> Université de Haute-Alsace, CNRS, IS2M, UMR 7361, F 68100, Mulhouse

<sup>c</sup> Université de Strasbourg, Strasbourg

<sup>d</sup> Aix-Marseille Université, CNRS, PIIM, UMR 7345, Centre de Saint Jérôme, 13013 Marseille

Les composés organochlorés aromatiques, comme le 1,2 dichlorobenzène (1,2-DCB), sont considérés comme des précurseurs de la formation de dioxines et leur élimination des gaz de combustion par adsorption pourrait être une solution. Les zéolithes de type FAU semblent les plus prometteuses car la taille des pores est comparable à la taille de certaines dioxines et composés chlorés [1, 2] et en particulier celles échangées avec des cations trivalents tels que Nd<sup>3+</sup>.

Dans cette étude, l'adsorption du 1,2 dichlorobenzène sur des billes de FAU-NaX et de FAU-NaX échangé au Nd<sup>3+</sup> est évaluée en utilisant une thermobalance dans des conditions dynamiques. Différents taux d'échange compris entre 11,4 et 53,6 % sont étudiés. Les billes de FAU sont entièrement caractérisées. Tous les échantillons sont activés à 400 °C pendant 2 heures sous azote avant l'adsorption de vapeurs organiques effectuée à 25 °C avec une pression relative de  $p/p^{\circ} = 0,5$ . Parallèlement, la variation de masse de chaque échantillon zéolithique a été enregistrée. A l'équilibre, les quantités de 1,2-DCB et d'eau adsorbées augmentent entre 284 et 324 mg/g avec l'augmentation du taux d'échange. Après adsorption, les échantillons sont analysés par un thermogravimètre couplée à un spectromètre de masse (TG/MS). La dérivée négative de la courbe de perte de masse montre 3 pics. Le premier pic situé à 80 °C correspond aux liaisons des atomes H du cycle aromatique du 1,2-DCB et de l'eau avec l'oxygène de la zéolithe : la position de ce pic ne varie pas avec le taux d'échange. Le second pic dont le sommet apparaît vers 130-160 °C correspond aux interactions électrostatiques entre l'eau et les cations de la zéolithe : sa température diminue de 160°C à 130 °C lorsque le taux d'échange augmente. Le troisième pic correspond aux interactions électrostatiques entre les électrons  $\pi$  du cycle aromatique et/ou des atomes de chlore du 1,2-DCB et les cations de la zéolithe. Cette température de désorption diminue de 380 à 310 °C avec le taux d'échange qui augmente. L'échange de zéolithes de type FAU avec des cations Nd<sup>3+</sup> semble prometteur pour thermo-désorber des composés chlorés aromatiques, comme les dioxines.

**Références :**

- [1] O. Schäfer, L. Tortet, A. Simon-Masseron, J. Patarin, S. Defour, R. Blanc, C. Coste, Y. Zerega, *Chemosphere* **259** 127457 (2020).  
[2] M. Mercury, N. Zouaoui, A. Simon-Masseron, Y. Zerega, C. Reynard-Carette, R. Denoyel, M. Carette, M. Souillard, A. Janulyte, J. Patarin, *Microporous and Mesoporous Materials* **177** 25–31(2013).

**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

**Comportement anti-osmotique de solutions aqueuses de perchlorate de sodium lors de l'intrusion à haute pression dans les zéosils hydrophobes**Amir Astafan<sup>a,b</sup>, Habiba Nouali<sup>a,b</sup>, Gérald Chaplais<sup>a,b</sup>, **Andrey Ryzhikov**<sup>a,b</sup><sup>a</sup> *Université de Haute-Alsace, CNRS, Institut de Science des Matériaux de Mulhouse (IS2M), UMR 7361, Axe Matériaux à Porosité Contrôlée, F-68100, Mulhouse, France Affiliation*<sup>b</sup> *Université de Strasbourg, F-67000 Strasbourg, France*

Les zéolithes purement siliciques (zéosils) à caractère hydrophobe présentent un grand intérêt pour les applications dans le domaine de l'absorption et du stockage d'énergie mécanique par intrusion-extrusion sous haute pression d'eau et de solutions salines aqueuses. L'utilisation de solutions salines concentrées permet d'augmenter considérablement les performances énergétiques de ces systèmes [1] en raison des phénomènes osmotiques ainsi que des énergies mises en jeu lors de la distorsion et de la déshydratation des ions solvatés durant l'intrusion. Dans le cas de systèmes « zéosil de type MFI – solution saline », il a été montré que la nature de l'anion de ces solutions salines a une forte influence sur le comportement énergétique et la pression d'intrusion [2]. Cependant, une des généralités majeures constatées réside dans le fait que la pression d'intrusion est toujours plus élevée que celle avec l'eau quel que soit l'anion étudié et augmente avec la concentration de sels pour toutes les zéolithes.

Ce travail porte sur l'intrusion-extrusion de solutions aqueuses de perchlorate de sodium dans les zéosils hydrophobes. Inversement aux résultats obtenus pour d'autres sels, la pression d'intrusion de solutions de  $\text{NaClO}_4$  dans le zéosil de type MFI (Silicalite-1, canaux 3D, ouverture de pores à 10 atomes Si) est toujours inférieure à celle d'eau (96 MPa) et diminue avec la concentration du sel. Pour la solution la plus concentrée avec le rapport molaire  $\text{H}_2\text{O}/\text{NaClO}_4 = 3,5$ , elle atteint un minima de 71 MPa. Ainsi, un comportement anti-osmotique de solutions aqueuses de perchlorate de sodium a été démontré. Une tendance similaire est observée pour le zéosil de type \*BEA (canaux 3D, ouvertures de pores à 12 atomes Si). Par contre, la pression d'intrusion de solutions de  $\text{NaClO}_4$  dans le zéosil de type CHA (chabazite, cages 3D, ouvertures de pores à 8 atomes Si) est toujours supérieure à celle d'eau et augmente avec la concentration du sel. Ainsi, l'effet anti-osmotique observé semble dépendre de la structure zéolithique. Cet effet est probablement lié à l'affinité d'ions de perchlorate envers la charpente zéolithique qui conduit à la diminution de la pression d'intrusion. L'impact de l'affinité semble être supérieur à celui des énergies de distorsion et de déshydratation des ions hydratés dans le cas des zéosils à pores larges ( $\geq 10$  atomes Si, MFI, \*BEA). Cependant, la situation s'inverse pour les zéosils à pores étroits (CHA), où l'énergie nécessaire pour la distorsion et la déshydratation des ions solvatés devient supérieure à celle de l'affinité.

**Références**[1] L. Tzani, M. Trzpit, M. Souillard, J. Patarin, *J. Phys. Chem. C* **116**, 20389 (2012).[2] T. Karbowski, C. Paulin, A. Ballandras, G. Weber, J.-P. Bellat, *J. Am. Chem. Soc.* **131**, 9898 (2009).



**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

**Performance of beta zeolite and beta catalyst in the catalytic cracking of model compound of Bio-Petroleum (sugar di-ketals)**

**D.Sc. Cristiane Cardoso (PG)<sup>a</sup>**, PhD. Yiu Lau Lam<sup>a</sup>, D.Sc. Juliana Carvalho<sup>a</sup>, D.Sc. Débora Nobrega<sup>a</sup>, D.Sc. Matheus Souza<sup>a</sup>, D.Sc. Alessandra Vieira<sup>a</sup> and D.Sc. Marcelo Maciel Pereira<sup>a</sup>.

<sup>a</sup> Federal University of Rio de Janeiro, Brazil.

The catalytic processes for producing hydrocarbons with higher added value in the refining and petrochemical industries are mostly elaborate with zeolites (Den Hollander *et al.*, 2002; Cejka, Morries and Nachtigall, 2017; Ibarra *et al.*, 2020). The application of zeolites is explained, more specifically, by their selectivity of products, avoiding unwanted parallel reactions and, consequently, inefficiency in the process. Therefore, by combining the potential of zeolite catalysts with the second-generation biomass conversion process into fuel under typical refinery conditions, a promising solution has emerged to reduce the carbon footprint. In this work, we explore two types of reactors, fixed bed (FB) and fluidized bed (FCC), the type of zeolitic catalyst processed with a model compound DX (1,2:3,5-di-O-isopropylidene- $\alpha$ -D-xylofuranose), representative of a bio-oil rich in carbohydrate acetals called Bio-Petroleum, and co-processed with n-hexane to produce biohydrocarbons. Concerning catalyst selection, firstly, fresh zeolites (Beta, ZSM-5, and USY) were first explored under conditions pre-established by the group. Beta Zeolite showed high performance in fixed bed in converting DX into hydrocarbons. In the best reaction condition, fresh Beta zeolite completely converted DX in the mixture containing 10% wt/wt DX in n-hexane produced a yield of 5.1% wt/wt aromatics in the liquid, 0.5% wt/wt in oxygenates and 1.8% wt/wt in coke. We point out the high formation of liquid products (using Beta) compared to USY and ZSM-5 zeolite (Batalha *et al.*, 2017; J. F. R. Pinto *et al.*, 2019; J. Pinto *et al.*, 2019; Cardoso *et al.*, 2023). Subsequently, two types of modifications were investigated. First, Beta was thermally treated using water vapor steam (to reduce the density of acidic sites). The best conversion to monoaromatics was obtained at 720°C, 5.5% wt/wt, reducing the gas yield twice and generating 1.3% wt/wt in coke. Second, we improved accessibility by creating mesoporosity. Beta with mesopores fully converted DX in more concentrated mixtures (30% DX mixture with n-hexane) and impaired by ten times the oxygenates in the liquid, increased liquid product ~3 times compared to the pristine Beta catalyst, also the coke did not exceed 4.9% wt/wt. To enable the FCC process, we used a catalyst containing Beta as the main active phase. The catalyst was thermally treated using previously optimized conditions. We used a cat/feed ratio of 3 (30 times more mass compared to the fixed bed), and reaction occurred at 540°C. We explored mixtures of DX from 10 to 70% in n-hexane. A mixture containing 70%DX incorporated ~77% of green carbon and hydrogen from DX into useful products (olefin, aromatics, furans, and cyclo-alkanes), in all cases we obtain high green carbons conversion into products. When correlating the FCC with the FB processes under similar conditions, the FCC process showed better performance, as it increased the liquid product and contributed to reducing the oxygenated compound. Thus, with the appropriate reaction parameters and modifications, Beta zeolite and Beta catalyst acted adequately in different types of reactors, demonstrating promise for the conversion of a renewable feedstock with a greater yield of carbon into Biohydrocarbons with high added value.

**Références**

- Batalha, N. *et al.* (2017) 'Biohydrocarbons Production under Standard Refinery Conditions by means of a Representative Ketal Compound of Biocrude', *Energy Technology*, 5(3), pp. 428–441. doi: 10.1002/ente.201600313.
- Cardoso, C. *et al.* (2023) 'Conversion of Sugar Di-Ketals to Bio-Hydrocarbons through Catalytic Cracking over Beta Catalysts in Fixed and Fluidized Catalytic Beds', *Chemistry*, 5(1), pp. 479–491. doi: 10.3390/chemistry5010035.
- Cejka, J., Morries, R. E. and Nachtigall, P. (2017) *Zeolites in Catalysis, Properties and Applications*. Royal Society of Chemistry. doi: 10.1039/9781788010610-00001.
- Den Hollander, M. A. *et al.* (2002) 'Gasoline conversion: Reactivity towards cracking with equilibrated FCC and ZSM-5 catalysts', *Applied Catalysis A: General*, 223(1–2), pp. 85–102. doi: 10.1016/S0926-860X(01)00745-1.
- Ibarra, Á. *et al.* (2020) 'A hybrid FCC/HZSM-5 catalyst for the catalytic cracking of a VGO/bio-oil blend in FCC conditions', *Catalysts*, 10(10), pp. 1–15. doi: 10.3390/catal10101157.
- Pinto, J. *et al.* (2019) 'Ketal Sugar Conversion Into Green Hydrocarbons by Faujasite Zeolite in a Typical Catalytic Cracking Process', *Frontiers in Chemistry*, 7(November), pp. 1–14. doi: 10.3389/fchem.2019.00720.
- Pinto, J. F. R. *et al.* (2019) 'Green-aromatic production in typical conditions of fluidized catalytic cracking', *Fuel*, 254(May), p. 115684. doi: 10.1016/j.fuel.2019.115684.

**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

**Nanosized zeolites for oxygen delivery and magnetic resonance imaging**

**Abdallah Amedlous<sup>a</sup>, Charly H elaine<sup>b</sup>, Oleg Lebedev<sup>c</sup>, Samuel Valable<sup>b</sup>, Svetlana Mintova<sup>\*a</sup>**

<sup>a</sup> *Normandie Universit , ENSICAEN, CNRS, Laboratoire Catalyse et Spectrochimie (LCS), 14050 Caen, France.*

<sup>b</sup> *Normandie Universit , UNICAEN, CNRS, ISTCT, GIP CYCERON, 14000 Caen, France*

<sup>c</sup> *Normandie Universit , ENSICAEN, UNICAEN, CNRS, Laboratoire de Cristallographie et Science des Mat riaux (CRISMAT), 14050 Caen, France.*

Glioblastoma is characterized by its high resistance to conventional treatments, such as radiation therapy and chemotherapy<sup>1</sup>. This is primarily due to the hypoxic environment, which is a major characteristic of glioblastoma<sup>2</sup>. 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 effects<sup>2</sup>.

Nanosized zeolites have emerged as a promising platform 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 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 agent (Na<sup>+</sup>) along with a phosphate buffer solution (PBS) as a clinical-grade solvent. By employing PBS instead of water, we successfully synthesized the zeolite crystals with desired chemical composition with nanoscale dimension 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 agent for magnetic resonance imaging (MRI). Importantly, our study highlights the enhanced safety profile of zeolite crystals at the nanoscale, paving the way for their broader application in biomedical research and clinical practice. Additionally, we explore the potential of nanosized FAU zeolite as an oxygen reservoir to rapidly release oxygen in the tumor microenvironment, thereby alleviating tumor hypoxia and enhancing radiotherapy. This zeolite nanocrystals holds the potential to serve as a platform for enhancing tumor oxygenation in anticancer therapy.

**References:**

- [1] R. Li, H. Wang, Q. Liang, L. Chen and J. Ren, *Biomater. Sci.*, 2022, **10**, 892–908.  
[2] C. Qiao, Z. Yang, X. Liu, R. Zhang, Y. Xia, L. Wang, Z. Chen, Q. Jia, R. Wang, Y. Yang and Z. Wang, *Nano Lett.*, 2022, **22**, 8250–8257.

**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

**Selective adsorption of NO<sub>x</sub> in presence of water by faujasite zeolite**

**E. P. Hessou,<sup>a,b</sup> A. Daouli,<sup>a</sup> W.G. Kanhounon,<sup>b</sup> H. Monnier,<sup>c</sup> M. Badawi<sup>a</sup>**

<sup>a</sup> *Laboratoire Lorrain de Chimie Moléculaire, UMR CNRS 7053, IUT de Moselle-Est, Saint-Avold, France*

<sup>b</sup> *Laboratoire de Chimie-Physique, Matériaux et Modélisation Moléculaire, Université d'Abomey-Calavi, Bénin*

<sup>c</sup> *INRS: Institut National de Recherche et de Sécurité, 1, rue du Morvan, 54519 Vandœuvre-lès-Nancy, France*

Emissions of diesel exhaust gas in confined work environments are a major health and safety concern, because of exposition to nitrogen oxides (NO<sub>x</sub>) [1]. Removal of these pollutants from exhaust gas calls for engineering of an optimum sorbent for the selective trapping of NO and NO<sub>2</sub> in the presence of water. Attention has been paid to water present in exhaust gas which can (1) compete with NO<sub>x</sub> removal; (2) react with NO<sub>2</sub> for producing NO and nitric acid [2]. Moreover, in the context of ecological transition, adsorbent regeneration also appears crucial. Thus, a subtle balance between high selectivity and easy regeneration is required.

In gas separation processes, we have chosen the adsorption technic to reduce the cost of the gas separation. Porous materials such as zeolites are known to be efficient adsorbents thanks to their capacity to exchange their charge-compensating cation, their structure, Si/Al ratio, high specific surface area, good thermal stability, shape selectivity, and relatively low cost. However, exploring experimentally zeolites with different Si/Al ratios and more than ten cations for example to identify the most promising formulation for an efficient separation/capture of NO<sub>x</sub> can be very time-consuming.

To overcome this problem, density functional theory (DFT) is one of the most efficient tools to describe adsorption processes in zeolites. Today, this method coupled with dispersion correction is accurate enough to predict adsorption energies and enthalpies for a number of molecules interacting with zeolites. Among the dispersion-corrected DFT methods we have shown that the TS/HI scheme which account for the ionic character of the zeolite provides better agreement with experiment [3]. After a screening of many monovalent and divalent cations, our theoretical results have allowed to identify Cu<sup>+</sup>, Ag<sup>+</sup>, Pt<sup>2+</sup> and Pd<sup>2+</sup> as promising cations to be exchanged in faujasite zeolite for the removal of NO<sub>x</sub> from exhaust gas in presence of water [4–5].

**References**

- [1] T. Lee, J. Park, S. Kwon, J. Lee and J. Kim, *Sci. Total Environ.* **461–462**, 377 (2013).  
[2] F. Delachaux, C. Vallières, H. Monnier, M.-T. Lecler, *Adsorption* **25**, 95 (2019).  
[3] F. Delachaux, E. P. Hessou, C. Vallières, H. Monnier, M. Badawi, *J. Environ. Chem. Eng.* **11** 109052 (2023).  
[4] E.P. Hessou, W.G. Kanhounon, D. Rocca, H. Monnier, C. Vallières, S. Lebègue, M. Badawi, *Theor. Chem. Acc.* **137**, 161 (2018).  
[5] A. Daouli, E. P. Hessou, H. Monnier, M-A. Dziurla, A. Hasnaoui, G. Maurin, M. Badawi, *Physical Chemistry Chemical Physics* **24**, 15565 (2022).



**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

**Optimization of Activation Conditions of supramolecular Metal-Organic Framework (MOF) for CO<sub>2</sub> Capture : Influence of solvent and temperature**

S. Feyziyeva<sup>a,b</sup>, N. Israfilov<sup>a,b</sup>, J. M. Planeix<sup>a</sup>, B. Louis<sup>b</sup>

<sup>a</sup> CMC UMR 7140, Université de Strasbourg, 4 rue Blaise Pascal, F-67000 Strasbourg, France.

<sup>b</sup> ICPEES UMR 7515, Université de Strasbourg, 25 rue Becquerel, F-67087 Strasbourg, France.

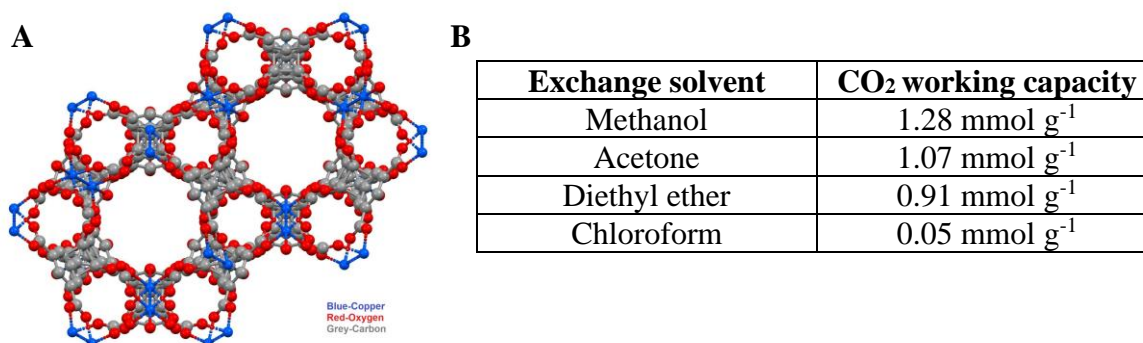
To fully exploit the porous capacity of materials, the removal of solvents from pores, referred to as activation, is crucial. Typically, rigid structures like zeolites and carbons are activated by direct heating at very high temperatures [1]. However, when dealing with MOFs, which are less rigid, careful attention must be paid to the activation temperature to prevent structural collapse. Therefore, to reduce the activation temperature, we opted for the exchange of a high-boiling solvent with a low-boiling-point alternative. However, this process becomes more complicated and interesting when MOF is supramolecular, such as SUM-103 [2].

Our study aimed to assess the influence of solvent exchange and activation temperature on the CO<sub>2</sub> adsorption capacity of SUM-103, a water-stable MOF based on copper paddlewheel SBUs (Secondary Building Units) synthesized with ethyleneoxy modified ligands.

The MOFs were immersed in four different solvents for 24 hours, with solvent exchange performed three times. Subsequently, activation was carried out at 160°C for 120 minutes under a nitrogen atmosphere. Thermogravimetric analysis was then conducted to determine CO<sub>2</sub> uptake capacity over 15 cycles between 30-100°C, and post-TGA, MOF stability was monitored by PXRD.

Among the solvents tested, methanol exhibited the highest CO<sub>2</sub> uptake performance at 160°C, yielding 1.28 mmol g<sup>-1</sup>. Chloroform displayed a significantly lower CO<sub>2</sub> uptake.

To find the optimal temperature for methanol-exchanged sample activation, temperatures of 80°C, 110°C, and 140°C were employed. The MOF demonstrated superior performance at 80°C, with a CO<sub>2</sub> uptake capacity of 1.32 mmol g<sup>-1</sup>.



**Fig. 1. A-** View from c axis of SUM-103. Side chains and hydrogen atoms were omitted for better visibility of pores; **B-** Working capacities of SUM-103 exchanged with different solvents and activated at 160°C;

**References**

[1]. A. R. Sujan, D.-Y. Koh, G. Zhu, V. P. Babu, N. Stephenson, A. Rosinski, H. Du, Y. Luo, W. J. Koros and R. P. Lively, *Ind. Eng. Chem. Res.*, 2018, **57**, 11757–11766.

[2]. N. Israfilov, K. Soukup, B. Louis and J.-M. Planeix, *New J. Chem.*, 2022, **46**, 8967–8970.

**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

**Intrusion sous haute pression de solutions aqueuses à base d'électrolytes chlorés dans ZIF-8 : influence de la nature du cation**

Amir Astafan,<sup>a,b</sup> Habiba Nouali,<sup>a,b</sup> Andrey Ryzhikov,<sup>a,b</sup> **Gérald Chaplais<sup>a,b</sup>**

<sup>a</sup> *Université de Haute-Alsace, CNRS, Institut de Science des Matériaux de Mulhouse (IS2M), UMR 7361, Axe Matériaux à Porosité Contrôlée, F-68100, Mulhouse, France*

<sup>b</sup> *Université de Strasbourg, F-67000 Strasbourg, France*

Depuis 2001, notre équipe étudie le procédé d'intrusion-extrusion de liquides non mouillants dans les matériaux poreux lyophobes pour l'absorption et le stockage de l'énergie mécanique [1,2]. Selon des paramètres physico-chimiques et structuraux divers, liés au matériau poreux combinés avec la nature de liquide non mouillant, le système « solide poreux–liquide non mouillant » est capable de restaurer, de dissiper ou d'absorber l'énergie mécanique fournie lors de l'étape d'intrusion et donc d'afficher respectivement un comportement ressort, amortisseur ou pare-chocs [1,2].

Les Zeolitic Imidazolate Frameworks (ZIFs), une sous-classe de Metal-Organic Frameworks (MOFs), peuvent posséder à la fois caractère hydrophobe et poreux requis pour une telle application. Le système « ZIF-8–eau » agit comme un ressort et est capable de stocker une énergie de 11-13 J/g avec une pression d'intrusion de 26 MPa [2,3].

L'énergie dépendant de la pression et du volume, une première étude a été menée pour augmenter la pression d'intrusion et l'énergie stockée dans les systèmes basés sur ZIF-8, avec l'utilisation de solutions aqueuses restreintes aux électrolytes comme LiCl, NaCl et KCl avec un rapport molaire eau/électrolyte proche de 14 [4].

Nos récents travaux d'intrusion sous haute pression ont été étendus à une plus large gamme de solutions aqueuses de sels chlorés de cations alcalins (LiCl, NaCl, KCl, RbCl, CsCl) proches de la saturation ou avec un rapport molaire eau/électrolyte de 12. Dans ce dernier cas, la pression d'intrusion ( $P$ ) augmente de 47 à 70 MPa avec la diminution du rayon cationique mais aussi celle de l'enthalpie d'hydratation du cation :  $P_{\text{Cs}^+} \approx P_{\text{Rb}^+} \approx P_{\text{K}^+} < P_{\text{Na}^+} < P_{\text{Li}^+}$ . Le comportement des systèmes « ZIF-8–solution aqueuses » est également affecté par la nature du cation électrolytique : systèmes de type ressort avec des énergies stockées de 19 J/g pour CsCl et RbCl, systèmes de type amortisseur avec des contributions pare-chocs pour KCl, NaCl et LiCl. Avec les solutions de RbCl et CsCl proches de la saturation, les tendances observées sont accentuées avec l'obtention de systèmes de type ressort pouvant stocker des énergies de 24 et 27 J/g avec des pressions d'intrusion de 59 et 67 MPa, respectivement.

**Références**

- [1] V. Eroshenko, R. Regis, M. Soulard, J. Patarin, *J. Am. Chem. Soc.*, **123**, 8129 (2001)  
[2] G. Ortiz, H. Nouali, C. Marichal, G. Chaplais, J. Patarin, *Phys. Chem. Chem. Phys.*, **15**, 4888 (2013)  
[3] A. Astafan, C. Dirand, A. Ryzhikov, H. Nouali, T. J. Daou, C. Marichal, J.-P. Bellat, I. Bezverkhy, G. Chaplais, *J. Phys. Chem. C*, **127**, 17249 (2023)  
[4] G. Ortiz, H. Nouali, C. Marichal, G. Chaplais, J. Patarin, *J. Phys. Chem. C*, **118**, 7321 (2014)

**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

## Understanding renewable hydrocarbon production from biomass using Beta zeolite

D. Santos,<sup>a</sup> C. Cardoso,<sup>a</sup> J. Carvalho,<sup>a</sup> M. Souza,<sup>a</sup> A. Vieira,<sup>a</sup> Y. Lam,<sup>a</sup> M. Pereira<sup>a</sup>.  
<sup>a</sup> *Federal University of Rio de Janeiro, Brazil*

Zeolites are important catalytic materials that play a key role in many processes. The Fluid Catalytic Cracking (FCC) and hydroconversion processes, which uses zeolites as catalysts, are the main processes in the oil refinery industry. Today, most fuels and energy are obtained from non-renewable sources, but environmental concerns in conjunction with the depletion of crude oil resources are becoming important factors encouraging the search for new raw materials. So, our group sought to solve this problem with a new process: converting this biomass (sugarcane bagasse) under mild temperature conditions on a semi-continuous flow process using acetone and an acid catalyst, producing an oil called biopetroleum, BP. BP is composed of sugar ketals, mainly 1,2:3,5-di-*O*-isopropylidene- $\alpha$ -D-xylofuranose (DX), and has favorable properties for use as a feed in a refinery of petroleum or in independent units.<sup>1</sup> The conversion of BP as well as DX by catalytic cracking, using Beta, ZSM-5 and USY zeolites as catalysts, mainly produces aromatics and light olefins, and the hydroconversion process, using Beta and ZSM-5 zeolites as catalysts, produces paraffins and naphthenics.<sup>2, 3</sup> In this work, the conversion of DX mixed with different hydrocarbons (n-hexane, cyclohexane, methylcyclohexane, and toluene) was studied in order to obtain information about the DX transformation pathway.<sup>4</sup> Initially, the DX mixture (10 to 20% by weight) with hydrocarbon was cracked by a Beta zeolite at a temperature of 500 °C in a fixed bed reactor. Tests with pure hydrocarbon were also carried out. Each test provided liquid (products, water, and unreacted hydrocarbon), gas and coke as products. The presence of DX reduced the hydrocarbon conversion, and depending on the hydrocarbons, the DX conversion decreased slightly. We interpret this result as a competition for the active sites following the order: n-hexane < cyclohexane < methylcyclohexane < toluene, where DX was completely converted in n-hexane and its conversion was 73% in toluene. In the presence of DX, hydrocarbons conversions were low, ranging from 3-10%. The hydrocarbons with increasing hydrogen transfer capacity, cyclohexane and methylcyclohexane, increased the yields of aromatics and naphthenics and the level of green carbon incorporated as useful products. The values were high: 73 and 78% by weight of C from DX were transformed into useful products in mixtures with cyclohexane and methylcyclohexane, respectively. Methylcyclohexane resulted in a much more significant increase in aromatics in the products than cyclohexane, being the preferred co-load to maximize aromatic products. Toluene is the most competitive for active sites and greatly reduces the transformation of DX and its derivatives. However, it can be used when seeking to obtain oxygenated intermediates. We observed that water was the first product of deoxygenation. Besides that, ketones and furanic derivatives were important intermediates for subsequent decarbonylation and decarboxylation, yielding hydrocarbons. DX reduced the hydrocarbon protolysis of both  $\sigma$ C-C and  $\sigma$ C-H bonds, decreasing the formation of H<sub>2</sub> and light hydrocarbons while the co-feed (and intermediates) contributed to the formation of aromatics, enabling a bimolecular reaction with oxygenates. The results will impact the design of more efficient and specific catalysts to BP conversion and new processes to increase green carbon into target products.

### Références

1. dos Santos, D. N.; Pedrosa, I. V.; Fernandes, C. R. R.; Lachgar, A.; Neli, M.; Garrett, R.; Lam, Y. L.; Pereira, M. M., Catalytic sugarcane bagasse transformation into a suitable biocrude for hydrocarbon production in typical refinery processes. *Sustainable Energy & Fuels* **2020**, *4* (8), 4158-4169.
2. Cardoso, C.; Lam, Y. L.; San Gil, R. A. S.; Van Bokhoven, J. A.; Pereira, M. M., Conversion of sugar diacetyls to bio-hydrocarbons by the catalytic cracking in a fixed bed with fresh and deactivated Beta zeolite. *Catalysis Communications* **2022**, *171*, 106519.
3. Souza, M. O.; Pereira, S. C.; Lau, L. Y.; Soter, L.; Pereira, M. M., Hydrodeoxygenation of Xylose Isopropylidene Ketal Over Pd/HBEA Catalyst for the Production of Green Fuels. *Frontiers in Chemistry* **2021**, *9*.
4. N. dos Santos, D.; J. F. S. Henrique, F.; Lam, Y. L.; Pereira, M. M., Understanding green-hydrocarbon production through the strategy of biomass ketalization reaction. *Sustainable Energy & Fuels* **2023**.



- 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

**THEME**

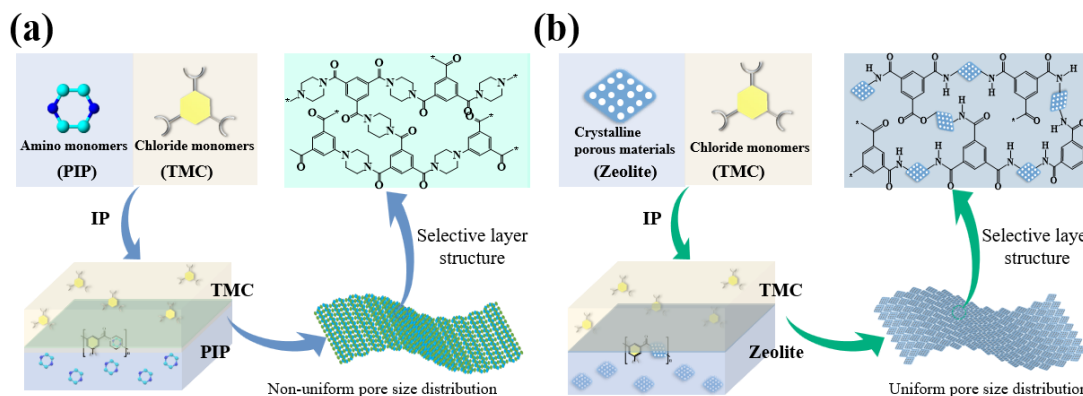
**Flexible Zeolite Membranes Based on Interfacial Polymerization Method**  
**Guodong Kong,<sup>a</sup> Zixi Kang<sup>b</sup> Hailing Guo<sup>a</sup>, Svetlana Mintova<sup>c</sup>**

<sup>a</sup> *State Key Laboratory of Heavy Oil Processing, China University of Petroleum (East China), Qingdao, Shandong, 266580, PR China.*

<sup>b</sup> *School of Materials Science and Engineering, China University of Petroleum (East China), Qingdao, Shandong, 266580, PR China*

<sup>c</sup> *Normandie Université, ENSICAEN, UNICAEN, CNRS, Laboratoire Catalyse et Spectrochimie (LCS), 14050 Caen, France*

Membrane separation technology has emerged as a vital means of separation in the chemical industry due to its advantages such as low energy consumption, pollution-free operation, and the ability to operate at ambient temperatures. Interfacial polymerization (IP) simplifies the preparation process and reduces production costs of polyamide membranes, making them widely applicable in drinking water purification, wastewater treatment, and mixed salt separation and purification. However, the lack of control during the IP process for polyamide membranes results in an uneven pore size distribution, making it challenging to achieve precise separation of ions and molecules with similar sizes. To address this issue, we propose employing stable and ordered crystalline porous materials (zeolite) for IP. Through the design of monomer structures and exploration of film-forming conditions, the modulation of the pore structure as well as the properties of the membranes were controlled, thus simultaneously improving the selectivity and permeability of the membranes.



**Fig. 1.** Schematic diagram of polyamide membrane (a) and flexible zeolite membrane (b) prepared by interfacial polymerization method.

**References**

[1] G. Kong, G. Yang, P. Xu, Z. Kang, H. Guo, M. Sun, Z. Yan, S. Mintova, D. Sun, Interfacial assembling of flexible silica membranes with high chlorine resistance for dye separation, *Journal of Membrane Science* 677 (2023) 121628. <https://doi.org/https://doi.org/10.1016/j.memsci.2023.121628>.

POSTERS  
THEME 3





## 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

## Mesure de coefficients de diffusion de l'eau dans des matériaux poreux par PFG $^1\text{H}$ NMR

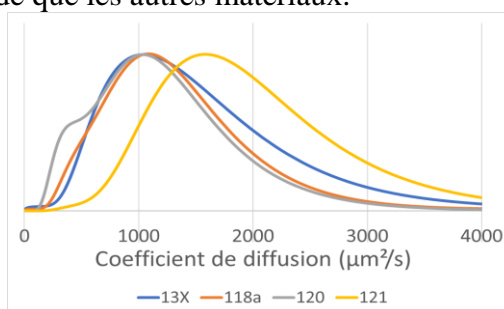
F. Bihl<sup>a</sup>, B. Vincent<sup>b</sup>, A-C. Roger<sup>a</sup>, B. Louis<sup>a</sup>,

<sup>a</sup> ICPEES – Université de Strasbourg, UMR 7515, 25 rue Becquerel, 67087 Strasbourg, France

<sup>b</sup> Institut de Chimie – Université de Strasbourg, 1 rue Blaise Pascal, 67000 Strasbourg, France

La quantification de la diffusion est cruciale dans de nombreux domaines, notamment celui du génie chimique dans l'optique d'optimiser les performances et les rendements des procédés. En milieu homogène et dans des conditions données, le phénomène de diffusion est caractérisé par le coefficient de diffusion  $D$  en  $\text{m}^2 \cdot \text{s}^{-1}$ . L'expression de  $D$  en milieu hétérogène comme par exemple au sein d'un solide poreux est bien plus complexe car il est nécessaire de parler des coefficients de diffusion pour représenter au mieux l'hétérogénéité des phénomènes de transport [1]. Ces coefficients sont fortement impactés par la taille et géométrie des pores ainsi que par les interactions entre les molécules mobiles et la paroi du solide. La résonance magnétique nucléaire (RMN) permet la mesure de coefficient de diffusion au sein de solide *via* l'application d'un gradient de champ magnétique pulsé [2].

Cette étude utilise la RMN pour déterminer les  $D$  de l' $\text{H}_2\text{O}$  à  $25^\circ\text{C}$  dans un solide aux micropores saturés en eau. Les matériaux étudiés sont une zéolithe 13X et les MOFs MIL-118a, MIL-120 et MIL-121. Les profils de diffusion mesurés montrent diverses diffusions correspondant aux molécules d'eau dans les différents pores (**Figure 1**). En prenant le sommet de la courbe comme coefficient d'auto-diffusion à  $25^\circ\text{C}$ , la valeur obtenue pour la zéolithe 13X est semblable à celles obtenues dans la littérature dans des conditions similaires [3-4]. De plus, la diffusion au sein du MIL-121 est 1,5 fois plus rapide que les autres matériaux.



**Fig. 1.** Profils des coefficients de d'auto-diffusion des matériaux poreux.

Malgré plusieurs prérequis tels que la connaissance des propriétés texturales ainsi que des mesures de diffusion avec différents paramètres d'analyse, la PFG  $^1\text{H}$  NMR permet d'obtenir des résultats fiables pour la caractérisation des matériaux poreux.

## Références

- [1] J. Kärger, *Adsorption*, **9**, 29-35 (2003).  
 [2] C. S. Johnson Jr., *Progress in Nuclear Magnetic Resonance Spectroscopy*, **34**, 203–256 (1999).  
 [3] P. Demontis, H. Jobic, M. A. Gonzalez *et al.*, *J. Phys. Chem. C*, **113**, **28**, 12373–12379 (2009).  
 [4] C. Parravano, J. D. Baldeschwieler, M. Boudart, *Science*, **155**, **3769** ; 1535-1536 (1967).



## 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

## Influence of ligands on position and coordination of cobalt cations in FAU zeolite

G. Medak,<sup>a</sup> F. Dalena<sup>a</sup>, D. Kuzman<sup>b</sup>, M. Cindrić<sup>b</sup>, S. Mintova<sup>a</sup>

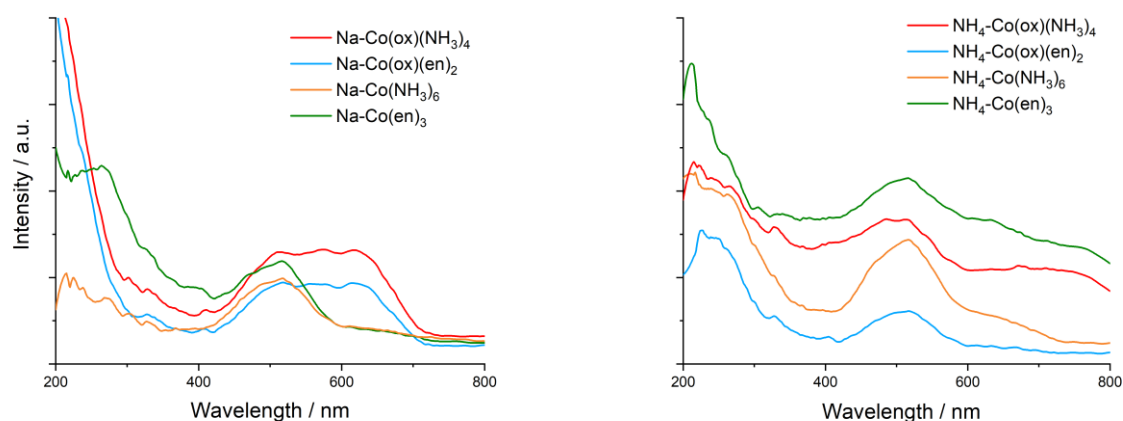
<sup>a</sup> LCS, ENSICEN, 6 Bd Maréchal Juin, Caen, France

<sup>b</sup> Faculty of Science, University of Zagreb, Horvatovac 102a, Zagreb, Croatia

E-mail: [glorija.medak@ensicaen.fr](mailto:glorija.medak@ensicaen.fr)

Cation exchange is one of the common ways to post-synthetically functionalize zeolitic materials. The classical procedure consists of exchange in water solution followed by calcination. Dissolving salts of transition metal cations in water results in the formation of aqua complexes of those cations. During the calcination process the water is removed and as the formed complexes break the cation gradually migrates to different sites in the zeolite framework.

By selecting different ligands (NH<sub>3</sub>, ethylenediamine-en, oxalate-ox) coordinated to the cobalt(III) we were able to determine how the coordination sphere of the metal cation (Co) and the dynamics of complex degradation affect the position of heteroatom in the zeolite framework after the calcination. The exchange was performed using zeolite Y prepared following the procedure described in the literature.[1] To avoid the formation of aqua complexes the cation exchange was performed by mechanochemical approach without additional use of water (only the water adsorbed in the zeolite was present). Powder XRD analysis showed no traces of cobalt oxide formation and the crystallinity of the samples was preserved. The influence of the zeolite features and different complexes on the coordination of cobalt(II) cation was characterized by solid state UV/vis spectroscopy (Fig. 1.). While the effect of cobalt(II) cation' coordination on the acid sites of the Y zeolite was determined by in situ FTIR spectroscopy using pyridine and deuterated acetonitrile probe molecules.



**Fig. 1.** Solid state UV/vis spectra of zeolite Y samples in sodium form (left) and ammonium form (right) after exchange with different cobalt(III) complexes after calcination

## Références

[1] S. Bosnar, D. Bosnar, N. Ren, N. Rajić, B. Gržeta, B. Subotić, *J. Porous Mater.* 2013, **20**, 1329-133

# LISTE DES PARTICIPANTS

<b>Nom</b>	<b>Prénom</b>	<b>Adresse électronique</b>
Aït-Oumeghar	Stéphane	marine.serralta@anton-paar.com
Abidi	Nawras	nawras.abidi@ifpen.fr
Al Atrach	Jaouad	jaouad.al-atrach@ensicaen.fr
Amedlous	Abdallah	abdallah.amedlous@ensicaen.fr
Barreau	Mathias	mathias.barreau@unicaen.fr
Batonneau-Gener	Isabelle	isabelle.gener@univ-poitiers.fr
Baudron	Stéphane	sbaudron@unistra.fr
Bellat	Jean Pierre	jean-pierre.bellat@u-bourgogne.fr
Benamar	Mohamed	mohamed.benamar@univ-poitiers.fr
Bieseki	Lindiane	lindiane.bieseki@gmail.com
Bihl	François	francois.bihl@etu.unistra.fr
Bloch	Emily	emily.bloch@univ-amu.fr
Bouchy	Christophe	christophe.bouchy@ifpen.fr
Bouillet	Raphaël	raphael.bouillet@saint-gobain.com
Bourgeois	Didier	didier.bourgeois@anton-paar.com
Castellã -Ventura	Martine	martine.ventura@lct.jussieu.fr
Chaib Draa	Yacine Malik	yacine-malik.chaib-draa@uha.fr
Chaouati	Nourrdine	nourrdine.chaouati@ensicaen.fr
Chaplais	Gérald	gerald.chaplais@uha.fr
Claessens	Benjamin	benjamin.claessens@univ-amu.fr
Clatworthy	Edwin	edwin.clatworthy@ensicaen.fr
Cochet	Damien	damien.cochet@bruker.com
Compère	Steven	steven.compere@univ-poitiers.fr
Comparot	Jean-Dominique	jean-dominique.comparot@univ-poitiers.fr
De Souza Cardoso	Cristiane	cristianesouza@iq.ufrj.br
Dalena	Francesco	francesco.dalena@ensicaen.fr
Daou	Jean	jean.daou@aptar.com
De Waele	Vincent	vincent.de-waele@univ-lille.fr
Del Cerro	Raphaël	raphael.delcerro@gmail.com
Denoyel	Renaud	renaud.denoyel@univ-amu.fr
Despoina	Andriotou	despoina.andriotou95@gmail.com
Devic	Thomas	thomas.devic@cnrs-imn.fr
Dhainaut	Jeremy	jeremy.dhainaut@univ-lille.fr
Dib	Eddy	eddy.dib@cnrs-orleans.fr

Dodin	Mathias	mathias.dodin@ifpen.fr
El Zayed	Maya	maya.el-zayed@ensicaen.fr
Fabbiani	Marco	marco.fabbiani@ensicaen.fr
Fahda	Mohammad	mohammad.fahda@ensicaen.fr
Faryssy	Mohamed	mohamed.faryssy@ribori-instrumentation.com
Fateeva	Alexandra	alexandra.fateeva@univ-lyon1.fr
Froehly	Marie	marie.froehly@uha.fr
Gaillard	Thomas	thomasmerias.79@gmail.com
Geloso	Marco Giuseppe	marco-giuseppe.geloso@ensicaen.fr
Ghojavand	Sajjad	sajjad.ghojavand@ensicaen.fr
Gilson	Jean-Pierre	jean-pierre.gilson@ensicaen.fr
Got	Clément	clement.got@ifp.fr
Guillet-Nicolas	Rémy	remy.guillet@ensicaen.fr
Hamacha	Rachida	rachidahamacha@gmail.com
Haonuan	Zhao	haonuan.zhao@ensicaen.fr
Hardy	Pauline	pauline.hardy@centralelille.fr
Honorato Piva	Diogenes	diogenes.honorato-piva@ensicaen.fr
Hu	Yue	hu.yue@ensicaen.fr
Hureau	Matthieu	matthieu.hureau@univ-lille.fr
Ibrahim	Maya	Maya.Ibrahim@saint-gobain.com
Israfilov	Nizami	nisrafilov@unistra.fr
Teixeira Da Silva	Antony	antonyjeova@gmail.com
Khadiri	Yassine	yassinekhadiri292@gmail.com
Kong	Guodong	guodong.kong@ensicaen.fr
Kouadio	Koffi Siméon	koffisimeonkouadio@gmail.com
Lakiss	Louwanda	louwanda.lakiss@ensicaen.fr
Le Person	Annaïg	annaig.le-person@univ-lille.fr
Legrand	Alexandre	alexandre.legrand@univ-lille.fr
Lemaitre	Thomas	Thomas.lemaitre@ensicaen.fr
Longue	Camille	camille.longue@ensicaen.fr
Louis	Benoit	blouis@unistra.fr
Ménard	Thomas	menardthomas.28@orange.fr
Magisson	Aymeric	aymeric.magisson@ensicaen.fr
Marta	Catarina	c.simao.marta@gmail.com
Martinez Franco	Raquel	raquel.martinez-franco@ifpen.fr

Medak	Glorija	glorija.medak@ensicaen.fr
Miqueu	Christelle	christelle.miqueu@univ-pau.fr
Moissette	Alain	alain.moissette@univ-lille.fr
Mussard	Léa	lea.mussard@univ-poitiers.fr
Nzodom	William	David-William's.NZODOMDJOZING@cea.fr
Oheix	Emmanuel	emmanuel.oheix@uha.fr
Ors	Taylan	taylan.ors@uha.fr
Pace	Ludovica	ludovica.pace@ensicaen.fr
Paillaud	Jean-Louis	jean-louis.paillaud@uha.fr
Payet	Frédéric	frederic.payet@aptar.com
Pinard	Ludovic	ludovic.pinard@ensicaen.fr
Plastiras	Orfeas	orfeas.plastiras@centralelille.fr
Premet	Laura	laura.premet@uha.fr
Reboul	Julien	julien.reboul@sorbonne-universite.fr
Risheng	Wang	rishengwang1006@gmail.com
Ruizhe	Zhang	ruizhe.zhang@ensicaen.fr
Ryzhikov	Andrey	andrey.ryzhikov@uha.fr
Sachse	Alexander	alexander.sachse@univ-poitiers.fr
Shabnam	Feyziyeva	shabnam.feyziyeva@etu.unistra.fr
Sigrist	Stephan	sigrist@onlinecas.com
Szitas	Pascal	Pascal.szitas@micromeritics.com
Talha	Zoulikha	talhazoulikha@yahoo.fr
Tortet	Laurence	laurence.tortet@univ-amu.fr
Valange	Sabine	sabine.valange@univ-poitiers.fr
Valtchev	Valentin	valentin.valtchev@ensicaen.fr
Volklinger	Christophe	christophe.volklinger@centralelille.fr
Wernert	Véronique	veronique.wernert@univ-amu.fr
Wu	Junwei	junwei.wu@ensicaen.fr
Xu	Jiani	jiani.xu@univ-lille.fr
Zerega	Yves	yves.zerega@univ-amu.fr

# ASSEMBLEE GENERALE

**Vendredi 29 mars 2024 à 09h45**

A l'issue du renouvellement des membres du Comité du GFZ par l'Assemblée Générale de l'association qui s'est tenue le 30 mars 2023, le nombre de personnes siégeant au Comité du GFZ était de 9, conformément aux statuts de l'association.

## Composition du comité :

- Benoît Louis (Membre), ICPEES – Strasbourg
- Christophe Bouchy (Secrétaire), IFPEN – Solaize
- Emily Bloch (Trésorière), Madirel – UMR 7246 – Marseille
- Alexandre Legrand (Membre), UCCS – Lille
- Rémy Guillet-Nicolas (Membre) LCS – UMR 6506 – Caen
- Louwanda Lakiss (Membre), LCS – UMR 6506 – Caen
- Alexander Sachse (Membre), IC2MP – Poitiers
- Andrey Ryzhikov (Membre), UHA – Mulhouse
- Stijn Van Daele (Membre), TotalEnergies – Feluy

L'assemblée devra procéder au remplacement ou renouvellement de trois membres du comité :

- Emily Bloch (Trésorière), Madirel – UMR 7246 – Marseille
- Stijn Van Daele (Membre), TotalEnergies – Feluy
- Louwanda Lakiss (Membre), LCS – UMR 6506 – Caen

Pour pouvoir au remplacement de ces membres sortants, le comité recevra les candidatures lors de la réunion du GFZ. Ces candidatures seront soumises au vote lors de l'Assemblée Générale. Les candidats sont priés de se faire connaître auprès d'un membre du bureau avant le jeudi 28 mars, 18 heures.

Le bureau du Groupe Français des Zéolithes remercie les sponsors pour leur participation.

