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Faculty of Science



**POROUS MATERIALS FOR
ENVIRONMENTAL APPLICATIONS 2024**

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BOOK OF ABSTRACTS

Miroslav Almáši (ed.)



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Edited by: **doc. RNDr. Miroslav Almáši, PhD.**, Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
miroslav.almasi@upjs.sk

Reviewed by:

Assoc. Prof. Satya Pal Nehra, Ph.D.,

Centre of Excellence for Energy and Environmental Studies, Deenbandhu Chhotu Ram University of Science and Technology, Murthal I-131039, India
spnehra.energy@dcrustm.org

Assoc. Prof. Virginie Hornebecq, Ph.D.,

Aix-Marseille University, CNRS, MADIREL, Centre de Saint J'érôme, Avenue Escadrille-Normandie-Niemen, F-133 97 Marseille, France
virginie.hornebecq@univ-amu.fr

Organisation Committee:

doc. RNDr. Miroslav Almáši, PhD.

Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
miroslav.almasi@upjs.sk

Mgr. et Mgr. Tomáš Zelenka, Ph.D.

Department of Chemistry, Faculty of Science, University of Ostrava, 30. Dubna 22, 702 00 Ostrava, Czech Republic
tomas.zelenka@osu.cz

RNDr. Milica Želinská, PhD.

Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
milica.fabisikova@upjs.sk

Ing. Michaela Halinkovičová

Slovenská chemická spoločnosť, Radlinského 9, 812 15 Bratislava, Slovak Republic
hospodarka@schems.sk



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	08:30 - 09:00	Prof. Hilda Elizabeth Reynel-Avila <i>Transforming Urban Waste into Energy: Preparation of Heterogeneous Catalysts to Produce Biodiesel</i> Laboratory of Water and Biofuels Engineering and Technology, Tecnológico Nacional de Mexico – Instituto Tecnológico de Aguascalientes, 20256, Aguascalientes, Mexico
	09:00 - 09:30	Assoc. Prof. Anshu Sharma <i>Graphitic Carbon Nitride-based Nanocomposites for Environmental Applications</i> Department of Physics, School of Engineering & Technology (SoET), Central University of Haryana, Mahendragarh 123031, India
	09:30 - 10:00	Dr. Dominika Capková <i>Metal-Organic Frameworks as Promising Hosts for Sulfur in Next-Generation Battery Technologies</i> Department of Chemical Sciences and Bernal Institute, University of Limerick, Limerick, V94 T9PX, Ireland
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	10:15 – 10:30	MSc. Samuel Kowalczyk <i>The Influence of the Flow Rate of the Inert Atmosphere During Pyrolysis on the Porosity of Carbonaceous Materials</i> Department of Chemistry, Faculty of Science, University of Ostrava, 30. Dubna 22, 702 00 Ostrava, Czech Republic
	10:30 – 10:45	Dr. Alžběta Parchaňská <i>Modification of the Preparation of Cellulose-based Porous Carbon Monoliths to Achieve Optimal Micro- and Mesoporosity</i> Department of Chemistry, Faculty of Science, University of Ostrava, 30. Dubna 22, 702 00 Ostrava, Czech Republic



- 10:45 – 11:00 **Assoc. Prof. Václav Slovák**
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Dubna 22, 702 00 Ostrava, Czech Republic
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Dubna 22, 702 00 Ostrava, Czech Republic
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Department of Chemistry, Faculty of Science, University of Ostrava, 30.
Dubna 22, 702 00 Ostrava, Czech Republic

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Chairman **Alžběta Parchaňská**

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Dubna 22, 702 00 Ostrava, Czech Republic
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Department of Chemistry, Faculty of Science, University of Ostrava, 30.
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Department of Inorganic Chemistry, Faculty of Science, P. J. Šafárik
University, Moyzesova 11, SK-041 01 Košice, Slovak Republic
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Laboratory of Advanced Materials, Department of Inorganic Chemistry,
University Institute for Advanced Materials, University of Alicante,
Alicante, Spain



14:00 – 14:15 **MSc. Meriem Abid**

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Laboratory of Advanced Materials, Department of Inorganic Chemistry, University Institute for Advanced Materials, University of Alicante, Alicante, Spain

14:15 – 14:30 **Dr. Ľuboš Zauška**

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Department of Inorganic Chemistry, Faculty of Science, P. J. Šafárik University, Moyzesova 11, SK-041 01 Košice, Slovak Republic

14:30 **Tomáš Zelenka**

CONFERENCE CLOSING



Invited Lectures



Organolanthanide Adsorbents: An Alternative for the Sequestration of Geogenic Pollutants from Water

D.I. Mendoza-Castillo^{a,b*}, F.G. Quintero-Álvarez^a, A. Bonilla-Petriciolet^a, M. Almáši^c

^a Laboratory of Water and Biofuels Engineering and Technology, Tecnológico Nacional de México – Instituto Tecnológico de Aguascalientes, 20256, Aguascalientes, Mexico

^b Researchers for Mexico, National Council of Humanities, Sciences and Technologies, 03940, Ciudad de México, Mexico

^c Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Safárik University in Košice, 04001, Kosice, Slovak Republic

*dimendozaca@conahcyt.mx

Fluoride and arsenic are relevant geogenic water pollutants in several countries [1, 2]. In Mexico, these contaminants are frequently found together in acuifers from different regions and it has been estimated that ~10.75 million people are affected by their exposure via drinking water [3]. The effective removal of these pollutants from water sources represents a significant environmental challenge and its relevant in terms of human health protection. This presentation analyzes the surface properties and adsorption efficacy of organolanthanide adsorbents (based on cerium, gadolinium, and ytterbium) for arsenic and fluoride removal. Adsorption equilibrium studies were performed at 20, 30, and 40 °C and pH 7. Some physicochemical characteristics of the adsorbents were determined by XRD, FTIR, SEM/EDX, N₂ physisorption, and XPS analyses. The equilibrium data were analyzed with statistical physics models to calculate steric parameters, and DFT calculations were utilized to characterize the adsorption mechanism and .pollutant-adsorbent interactions.

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References

- [1] S.V. Jadhav, E. Bringas, G.D. Yadav, V.K. Rathod, I. Ortiz, K.V. Marathe, *J. Environ. Manage.* **162** (2015) 306-325.
- [2] M. Kumar, R. Goswami, A.K. Patel, M. Srivastava, N. Das, *Chemosphere* **249** (2020) 126126.
- [3] M.T. Alarcón-Herrera, D.A. Martín-Alarcon, M. Gutiérrez, L. Reynoso-Cuevas, A. Martín-Domínguez, M.A. Olmos-Márquez, J. Bundschuh, *Sci. Total Environ.* **698** (2020) 134168.



Graphitic Carbon Nitride based Nanocomposites for Environmental Applications

A. Sharma

Department of Physics, School of Engineering & Technology (SoET), Central University of Haryana, Mahendragarh 123031, India

anshuphysics@cuh.ac.in

Graphitic carbon nitride (gCN), a metal-free photocatalyst, has drawn considerable interest because of its possible use in photocatalytic environmental pollution treatment. The findings show that, rather than changing the sample crystalline structure, this extensively disperses gCN to increase its surface area. This work represents the combination of tungsten oxide doped gCN, also known as $\text{WO}_3@g\text{-C}_3\text{N}_4$ (WCN) and in situ selenium-doped graphitic carbon nitride, also known as $\text{Se-g-C}_3\text{N}_4$ (SCN), which are synthesized by employing inexpensive urea and tungsten oxide powder as precursor materials. SEM (scanning electron microscopy), XRD (X-ray diffraction), FTIR (Fourier-transform infrared spectroscopy), as well as TGA (Thermogravimetric analysis) was utilized to describe the morphological, optical and structural characteristics of the treated photocatalyst. Three different photocatalytic composites of SeNPs and $g\text{-C}_3\text{N}_4$ in the mass ratios of 1:1, 2:1, and 3:1, denoted SCN1, SCN2, and SCN3, were created for the methylene blue (MB) and methyl orange (MO) photodegradation. The combined photocatalytic degradation rate of MB after 150 minutes in visible light (500-800 nm) was 75.4% for SCN1, 87.8% for SCN2, and 81.3% for SCN3. For MO, the photocatalytic activity of produced materials was also investigated. The analysis's outcome reveals astonishing deterioration values for SCN1 (62.5%), SCN2 (74.1%), and SCN3 (68.5%), respectively. Similarly, three different photocatalytic composites of tungsten oxide and gCN in the mass ratios of 1:1, 2:1, and 3:1, denoted WCN1, WCN2 and WCN3 were created for the MB and MO photodegradation. The combined photocatalytic degradation rate of MB after 150 minutes in visible spectrum (500-800 nm) was 52.46% for gCN, 86.4% for WCN1, 98.8% for WCN2, and 91.2% for WCN3. For MO, the generated materials' photocatalytic activity was examined. The analysis outcome reveals astonishing deterioration values for WCN1 (72.9%), WCN2 (89.7%), and WCN3 (83.6%), respectively. The hybrid photocatalyst produced stable photodegradation performance for five cycles. The heterojunction WCN and SCN photocatalyst is a promising visible light active material for the treatment of pharmaceuticals and dyes in water using the photocatalysis process.

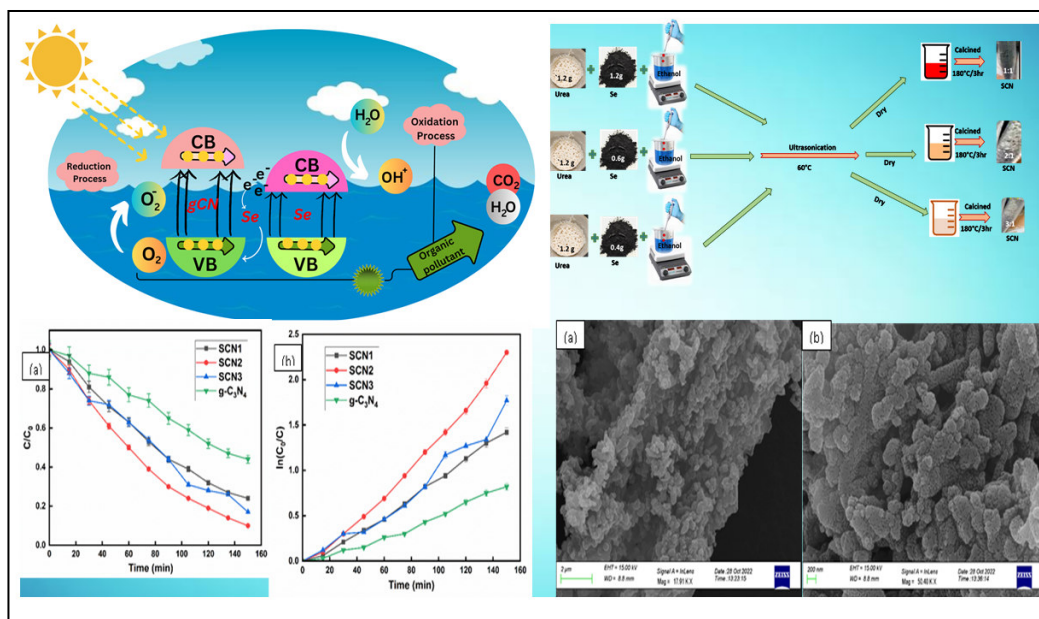


Figure 1 Synthesis, Morphology and Photodegradation of gCN and SCN.



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References

- [1] V Zhurenok, T.V. Larina, D.V. Markovskaya, S.V. Cherepanova, E.A. Mel, E.A. Kozlova, Ital. Oral Surg. **31** (2021) 157-159.
- [2] D.R. Paul, R. Sharma, P. Panchal, S.P. Nehra, A.P. Gupta, A. Sharma, Int. J. Hydrogen Energy. **45** (2020) 23937-23946.



Metal-Organic Frameworks as Promising Hosts for Sulfur in Next-Generation Battery Technologies

D. Capkova^{a*}, T. Kazda^b, N. Király^c, A. Straková Fedorková^d, K.M. Ryan^a, M. Alnáši^c

^a Department of Chemical Sciences and Bernal Institute, University of Limerick, Limerick, V94 T9PX, Ireland

^b Department of Electrical and Electronic Technology, Faculty of Electrical Engineering and Communication, Brno University of Technology, Technická 10, 616 00 Brno, Czech Republic

^c Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

^d Department of Physical Chemistry, Faculty of Sciences, Pavol Jozef Šafárik University in Kosice, Moyzesova 11, 040 01 Košice, Slovak Republic

*Dominika.Capkova@ul.ie

The dynamic development of modern society has created a high energy demand, especially for portable electronic devices, the automotive industry, and aerospace. The main challenge is storing electric energy effectively and safely [1, 2]. Rechargeable lithium-ion (Li-ion) batteries have become indispensable energy storage devices due to their high safety. However, their specific energy density based on the intercalation process is insufficient for future applications. As an alternative to Li-ion batteries, the conversion mechanism of lithium-sulfur (Li-S) batteries became the target of intensive research. Li-S batteries are considered a candidate for next-generation energy storage systems due to their high theoretical energy density (2600 Wh kg⁻¹), low sulfur cost, and environmental compatibility [3].

In this work, various MOF materials are tested as support for sulfur in Li-S batteries. MOFs have different structures and organic linkers are connected via different metal ions. The structure of activated MOF-76(Gd) showed the lowest capacity fade per cycle despite 50 cycles during the rate capability test. In an effort to improve the electrochemical properties, MOFs were carbonized. It was proven, that the carbonization process of MOF enhanced its properties and the electrode material showed highly stable cycle performance. Overall, the best electrochemical properties, the highest discharge capacities, and stable cycle performance showed carbonized MOF-76(Gd).

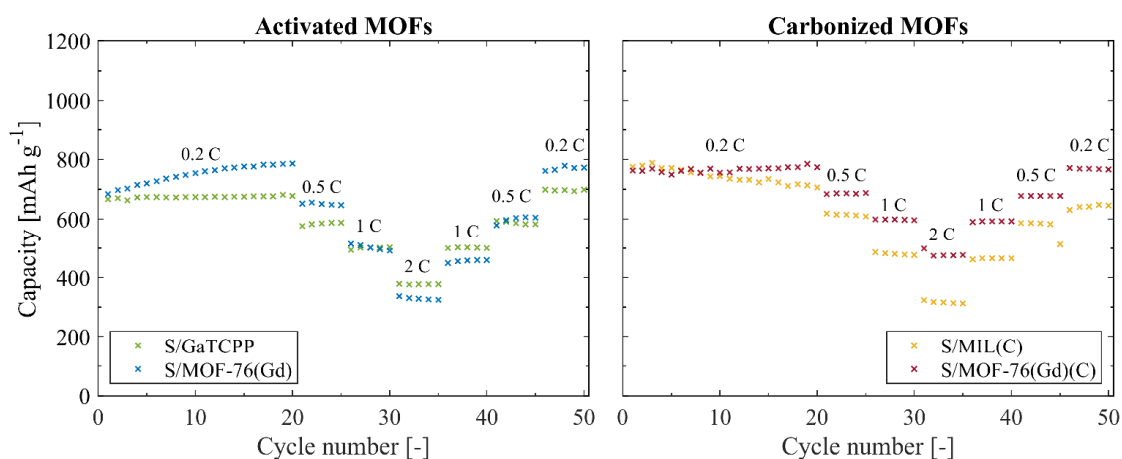


Figure 1 Galvanostatic cycling of different activated and carbonized MOFs at various C-rates.

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References

- [1] Y. Zheng, S. Zheng, H. Xue, H. Pang, *J. Mater. Chem. A* **7** (2019) 3469–3491.
- [2] V. Knap, D.-I. Stroe, *J. Power Sourc.* **498** (2021) 229913.
- [3] D. Capkova, T. Kazda, O. Cech et al., *J. Energy Stor.* **51** (2022) 104419.



Tetrazine-based MOFs: Structural Diversity and Versatile Covalent Functionalization

G. Kowacz, M. Ryndak, D. Jędrzejowski, D. Matoga*

Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Kraków, Poland

*dariusz.matoga@uj.edu.pl

Metal-organic frameworks (MOFs) are a large group of materials characterized by their crystallinity, modular structures and porosity [1]. These features provide unique opportunities to design and study them for a variety of applications, such as catalysis, gas storage and separation, chemical sensing, drug delivery or energy storage and conversion. Targeted properties of MOFs can be achieved by assembling appropriate molecular building blocks or by using post-synthetic modifications that are often unavailable in direct synthesis.

The talk will present our latest research on the incorporation of the s-tetrazine motif into MOF structures making them amenable to covalent modification and diverse functionalization. Representative covalent modifications of the MOFs encompass inverse electron-demand Diels-Alder (iEDDA) reactions with numerous dienophiles to enhance stability, tune porosity and induce proton conduction, to name a few. Our original tetrazine-based platforms (JUKs) selected for discussion will include flexible structures with a linear N-donor linker [2], rigid frameworks with di- and tetra-topic polycarboxylate linkers, and materials that form spherulite superstructures with the characteristic Maltese cross observed under polarized light [3]. Multistep synthetic pathways, different types of structures as well as properties of pristine and modified materials, will be discussed. Finally, possible future research directions involving tetrazine-based JUKs will be indicated.

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References

- [1] R. Freund, S. Canossa, S.M. Cohen, W. Yan, H. Deng, V. Guillerme, M. Eddaoudi, D.G. Madden, D. Fairen-Jimenez, H. Lyu, L.K. Macreadie, Z. Ji, Y. Zhang, B. Wang, F. Haase, C. Wöll, O. Zaremba, J. Andreo, S. Wuttke, C.S. Diercks, *Angew. Chem. Int. Ed.* **60** (2021) 23946-23974.
- [2] D. Jędrzejowski, M. Pander, W. Nitek, W. Bury, D. Matoga, *Chem. Mater.* **33** (2021) 7509-7517.
D. Jędrzejowski, M. Ryndak, J.J. Zakrzewski, M. Hodorowicz, S. Chorazy, D. Matoga, *ACS. Appl. Mater. Interfaces* **15** (2023) 25661-25670.
- [3] G. Kowacz, M. Ryndak, D. Jędrzejowski, D. Matoga, et al. unpublished work.



Transforming Urban Waste into Energy: Preparation of Heterogeneous Catalysts to Produce Biodiesel

H.E. Reynel-Ávila^{a,b*}, B.P. Escalera-Velasco^a, M.L. Malagón-Quinto^a, F.J. Villalobos-Delgado^a, A. Bonilla-Petriciolet^a, M. Almáši^c, C. Durán-Valle^d

^a Laboratory of Water and Biofuels Engineering and Technology, Tecnológico Nacional de México – Instituto Tecnológico de Aguascalientes, 20256, Aguascalientes, Mexico

^b Researchers for Mexico, National Council of Humanities, Sciences and Technologies, 03940, Ciudad de México, Mexico

^c Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Safárik University, 04001, Kosice, Slovak Republic

^d IACYS, University of Extremadura, Badajoz, 06006, Spain

*hereynelav@conahcyt.mx

The main challenge in the production and commercialization of biofuels, particularly in low-income countries, is the high cost of raw materials, especially when edible feedstocks are utilized [1]. As example, the cost of inputs such as oils and catalysts to obtain biodiesel accounts for approximately 70-80% of its final production price [2]. Therefore, the valorization of local urban wastes is crucial from both economic and environmental aspects, offering a viable resource for the generation of low-cost bioenergy [3]. In this presentation, we describe a circular economy approach to produce low-cost biodiesel using urban wastes such as Tetra Pak, cigarette filters, and avocado seed as precursors of solid catalysts and Mexican biomass wastes as lipidic sources. Three case studies will be discussed to show the competitive performance of the catalysts to produce biodiesel: 1) A catalyst derived from TetraPak, 2) A magnetic catalyst derived from cigarette filter wastes, and 3) A catalyst from metal-organic compounds supported on a char derived from avocado seed. The best preparation conditions of these catalysts were identified via the Signal/Noise ratio analysis. Transesterification kinetics were determined and modeled to obtain kinetic parameters and activation energy. Catalysts reuse was also tested. Biomass, catalysts, and reaction products were characterized using several instrumental techniques such as FTIR, ICP, XRD, EDX-SEM, WDXRF, XPS, and N₂ adsorption-desorption isotherms. All the catalysts showed competitive performance.

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References

- [1] R. Intasit, B. Cheirsilp, Y. Louhasakul, P. Boonsawang, *Bioresour. Technol.* **315** (2020) 123893.
- [2] A. Al-Saadi, B. Mathan, Y. He, *Chem. Eng. Res. Des.* **162** (2020) 238-248.
- [3] A. Arora, V. Singh, *Appl. Energy* **280** (2020) 115933.



Lectures and Posters



From Basic Research to Commercial Applications: Challenges and Opportunities in Separation Technologies

M. Dudák

ANAMET s.r.o., Kováků 3210/26, 150 00, Praha 5, Czech Republic

dudak@anamet.cz

I hope this interdisciplinary discussion will provide new insights into the commercialization potential of basic research, especially in the field of material sciences. My perspective is shaped by an academic foundation in reactor engineering, which I acquired through a Ph.D. from the University of Chemistry and Technology in Prague. This was further enhanced by my experience at the Johnson Matthey Research Centre in the UK. Currently, in my role at ANAMET s.r.o., I have spent the last nine years supporting customers in the application of porous and catalytic materials, giving me a practical, sales-oriented view of the industry.

In the Czech Republic, there are numerous groups of synthetic chemists developing innovative materials, often based on fundamental research. However, the transition from these research ideas to commercially viable products has been limited. One of the primary challenges is the need to move beyond the characterization of pure components to understanding the behavior of mixtures in real-life applications. Two primary separation technologies are under consideration: membranes and adsorption columns.

For gas separation, inorganic membranes pose significant preparation challenges, such as achieving homogeneity across large areas and withstanding operational conditions. Despite these obstacles, there are opportunities for collaboration with commercial partners for testing. The 4A zeolite project, which targets ethanol purification by leveraging differential adsorption strengths, exemplifies the importance of studying mixture behavior in the development of functional materials.

In adsorption columns, Pressure Swing Adsorption (PSA) and Temperature Swing Adsorption (TSA) are the most common regeneration schemes, with Simulated Moving Bed (SMB) technologies offering a promising alternative. The most anticipated large-scale application of these technologies is carbon capture, with subsequent storage or utilization.

On a smaller scale, tailored porosity in catalysts allows specific reactants to access the catalyst active sites while enabling products to exit the catalyst particle, demonstrating a 'sieving effect'. An example could be selective CO oxidation catalyst for CO removal from recycle stream in the maleic anhydride synthesis from *n*-butane over vanadyl pyrophosphate catalyst.

To bridge the gap between basic research and practical applications, it's essential to focus on characterizing the behavior of complex mixtures and collaborating with commercial partners for testing and scaling up. I will also present characterization tools and techniques that can support these developments, along with examples of successful technology implementations and potential applications.



MOF-Carbon Composite Materials for Carbon Dioxide Sorption

A. Badač^{a*}, T. Zelenka^a, M. Almáši^b, J. Holub^a, G. Zelenková^a, B. Taraba^a, L. Zauška^b

^aDepartment of Chemistry, Faculty of Science, University of Ostrava, 30. Dubna 22, 702 00 Ostrava, Czech Republic

^bDepartment of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

*Badaal41@osu.cz

The paper is focused on the method of preparation of MOF-carbon composite material (MOF@HPCM), which can be used as an effective material for adsorption and storage of carbon dioxide in the future.

A hierarchically porous carbon monolith (HPCM) [1] with a suitable surface treatment was used for the preparation of the composite material, in the pores of which MOF materials – HKUST-1 (Cu), MOF-76 (Gd) and MIL-101 (Fe) were crystallized. Characterization of composites using scanning electron microscopy (SEM) and subsequent Thermogravimetric analysis (TG) confirmed the presence of MOF materials. The parent materials and the resulting composites were subjected to carbon dioxide sorption at 273 K to obtain the adsorbed amount and then at 288 K and 303 K to calculate isosteric heat ($-Q_{\text{ISO}}$).

Sorption experiments showed the most promising composite HKUST-1 (Cu)@HPCM-OH, whose sorption capacity at 273 K increased from 1.87 mmol/g to 2.42 mmol/g compared to the original material (HPCM-OH), while the isosteric heat ($-Q_{\text{ISO}}$) remained almost unchanged compared to the parent material – 30.65 kJ/mol for HPCM-OH and 29.66 kJ/mol for HKUST-1 (Cu)@HPCM-OH. More detailed information will be presented in the form of a poster.

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References

[1] P. Bulavová, J. Parmentier, V. Slovák, *Microp. Mesop. Mater.* **272** (2018) 155-165.



Modification of the Preparation of Cellulose-based Porous Carbon Monoliths to Achieve Optimal Micro- and Mesoporosity

A. Parchaňská^{a*}

^a Přírodovědecká fakulta, Ostravská Univerzita, 30. dubna 22, 701 03 Ostrava

*alzbeta.parchanska@osu.cz

Porous carbonaceous materials find applications in many fields, including water treatment, catalysis or supercapacitor fabrication. Numerous organic precursors can be used as sources of carbon. Due to the increasing demand for environmentally friendly methods based on renewable starting materials, several processes have been developed to prepare porous carbonaceous materials, using microcrystalline cellulose as the carbon source.

The simple pyrolysis of microcrystalline cellulose powder, often in the presence of a specific activator, produces porous carbon powder. However, porous carbon monoliths, which are particularly suitable for adsorption from liquid phases, are attracting increasing attention. After adsorption, they can be easily removed from the liquid medium, making them more practical for this application.

The first step in preparing a cellulose-based carbonaceous monolith is converting powdered microcrystalline cellulose into a liquid phase or solution. One of the simplest methods involves dissolving cellulose in a cooled aqueous solution of sodium hydroxide^{1, 2}. After freezing this solution in appropriate molds, which shapes the monoliths and forms some of the pores through ice-templating³, water is removed by ethanol regeneration or lyophilization. During this process, cellulose is precipitated, and in the case of lyophilization, additional pores are created. Subsequently, sodium hydroxide is removed by repeated washing with deionized water. The final preparation steps include drying the monoliths and subjecting them to pyrolysis in an inert nitrogen atmosphere.

This method of preparing carbonaceous monoliths from cellulose is relatively time-consuming^{1, 2}. Another drawback is the predominantly microporous structure of these monoliths, with most pores having diameters of less than 2 nm². While the presence of micropores increases the specific surface area of the monoliths and enhances adsorption capacity, effective transport of adsorbates in water treatment and electrochemical applications requires the presence of mesopores (2–50 nm in diameter) or macropores (greater than 50 nm). To form an adequate amount of mesopores and macropores, it is essential to optimize all stages of carbonaceous monolith synthesis—from microcrystalline cellulose particle size to final drying and pyrolysis—since each step can influence the porosity of the final product.

The formation of mesopores is also enhanced by doping the monoliths with iron, typically in the form of ferrous salt¹. Additionally, iron doping results in magnetic porous carbon monoliths, as most of the added ferrous salts are reduced to metallic iron during pyrolysis.

The goal of the present study is to modify the established method^{1, 2} of preparing cellulose-based porous carbon monoliths doped with iron to optimize both micro- and mesoporosity without extending the overall time required for the procedure. Each step of the synthesis can be adjusted. Recently, the regeneration step was altered by replacing ethanol regeneration with lyophilization.

In the present work, two additional steps of the procedure were modified: (1) freezing the solution and (2) drying the monoliths before pyrolysis. Two different ways of freezing, (i) freezing in the freezer at -10 °C and (ii) freezing in liquid nitrogen at -196 °C, were tested. Another modification involved heating the cellulose solution in the molds to 85 °C for 1 hour prior to the both freezing methods.

Two different ways of drying the monoliths before pyrolysis, (i) drying at 80 °C and (ii) lyophilization, were tested.

All the modified procedures, along with respective sample names, are summarized in Table 1.

The porosity of prepared monoliths was characterized by nitrogen sorption. The chemical composition of monoliths was characterized by Raman spectrometry and the crystalline phases were characterized by X-ray diffraction (XRD). The texture of the monoliths was examined by high resolution transmission electron microscopy (HR-TEM).



It was found that freezing in liquid nitrogen, without previous heating to 85 °C, resulted in the monoliths with the highest specific surface area and the highest mesopore volume. Drying by lyophilization introduced additional micropores.

According to the XRD, all the monoliths have similar chemical composition: the main portion is constituted by carbon (in the form of graphite, multilayer graphene and amorphous carbon). Iron is present mainly in the form of metal iron and, to the less extent, in the form of iron carbide (cohenite, Fe₃C) and in the form of magnetite (Fe₃O₄). In the HR-TEM images (Figure 1), many iron/iron carbide nanoparticles surrounded by multilayer graphene structures are visible. Ring-shaped multilayer graphene structures without particle in the center are also visible. These structures are supposed to create substantial part of mesopores.

Freezing in liquid nitrogen is therefore the most promising modification and a starting point for a further method development.

Table 1: List of all prepared samples

Sample name	heating to 85 °C	freezing	drying
CMG Fe 1-1	No	Freezer (-10 °C)	Dryer
CMG Fe 1-2	No	Freezer (-10 °C)	Lyophilization
CMG Fe 2-1	No	Liquid nitrogen (-196 °C)	Dryer
CMG Fe 2-2	No	Liquid nitrogen (-196 °C)	Lyophilization
CMG Fe 3-1	Yes	Freezer (-10 °C)	Dryer
CMG Fe 3-2	Yes	Freezer (-10 °C)	Lyophilization
CMG Fe 4-1	Yes	Liquid nitrogen (-196 °C)	Dryer
CMG Fe 4-2	yes	Liquid nitrogen (-196 °C)	lyophilisation

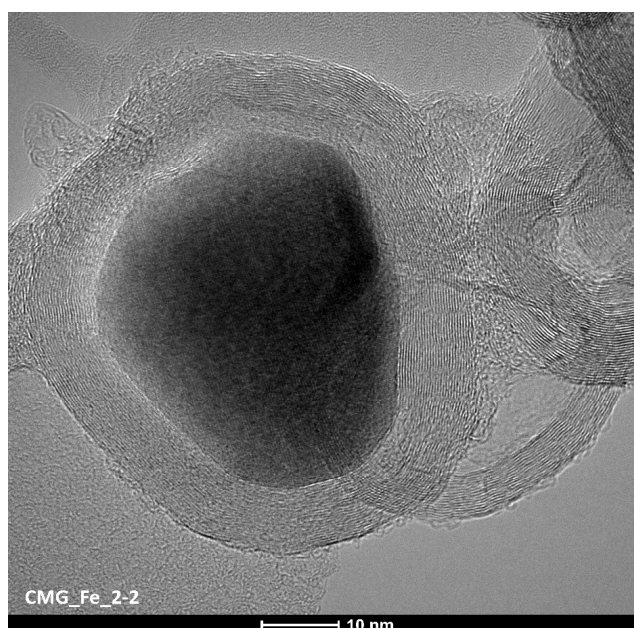


Figure 1 HR-TEM image of sample CMG_Fe_2-2 (frozen in liquid nitrogen and dried by lyophilisation).

Acknowledgements

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References

- [1] M.P. Chavhan, A. Kryeziu, S. Ganguly, J. Parmentier, *Green Carbon* **2** (2024) 109.
- [2] A. Kryeziu, V. Slovák, J. Parmentier, T. Zelenka, S. Rigolet, *Indust. Crops Prod.* **183** (2022) 114961.
- [3] F. Bouville *et al.*, *J. Am. Chem. Soc.* **97** (2014) 1736.



Insight into Energetics of Carbon Dioxide Adsorption on „HPCM@MOF“ Composites

B. Taraba*, T. Zelenka, A. Badač

Department of Chemistry, Faculty of Science, University of Ostrava, 30. Dubna 22, 702 00 Ostrava, Czech Republic

*boleslav.taraba@osu.cz

Calorimetric (Setaram C80, France) and adsorption (Quantachrome Instruments, Autosorb iQ-XR, USA) measurements were performed to study energetics and reversibility of the adsorption of CO₂ on „Carbon@MOF“ (HPCM-OH@HKUST-1) composites. Using calorimetry, good reversibility of the adsorption/desorption cycle of CO₂ was approved, ranging from 83 to 99%. Adsorption (integral) heat of CO₂ on carbonaceous surface (sample HPCM-OH) was determined to be 29.1 kJ/mol, which is by ca 10%_{rel} higher than that on surface of the MOF (HKUST-1) reaching value of 26.2 kJ/mol. On the other hand, adsorbed amount of carbon dioxide on HKUST-1 markedly exceeds that on HPCM-OH (exactly, 3.6 mmol CO₂/g for HKUST-1 in comparison with 0.61 mmol CO₂/g for HPCM-OH). The adsorption heats of the calorimetric measurements were found to be well comparable with mean values of the isosteric adsorption heat as ascertained from the adsorption isotherms of CO₂ at temperatures 273 K, 288 K and 303 K.

Acknowledgement

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Interface Phenomena in Carbon-TiO₂ Composites: Heteroatom-Driven Photocatalytic Advancements for Sustainable Applications

C. Abreu-Jaureguí*, A. Sepúlveda-Escribano, J. Silvestre-Albero

Laboratorio de Materiales Avanzados, Dpto. Química Inorgánica, Instituto Universitario de Materiales Avanzados, Universidad de Alicante, Alicante, España

*coset.abreu@ua.es

Surface chemistry plays a fundamental role in the photodegradation interplay, wherein heteroatoms such as nitrogen, phosphorus, and oxygen serve as mediators to enhance the electronic properties of the composite and facilitate the creation of active sites within the catalyst's surface [1]. In this context, carbon-TiO₂ composites are the go-to basis for validating their true ability to improve their photocatalytic performance [2]. Our investigation focused on modulating carbon nanotubes with oxygen, nitrogen, or phosphorous, enriching P25 through meticulously tailored chemical pathways and wet impregnation with methanol [3]. Techniques such as TGA-MS helped to elucidate the nature of functional groups in the composites. At the same time, XPS and Raman spectroscopy revealed an interesting interface phenomenon suggesting enhanced electron-hole mobility at the nanotube/TiO₂ interface, especially for TiO₂/OSWCNT and TiO₂/PSWCNT catalysts. Notably, these catalysts displayed an exceptional performance, achieving near-complete degradation of Rhodamine B under simulated solar irradiation within two hours. Furthermore, cyclability tests with our flagship catalysts confirmed their enduring performance over five cycles, with swift regeneration facilitated via methanol/water extraction. Overall, these findings provide a valid reference point for any future utilization of heteroatoms like nitrogen, oxygen, and phosphorous to enhance photocatalytic activity in oxidation reactions toward a cleaner future.

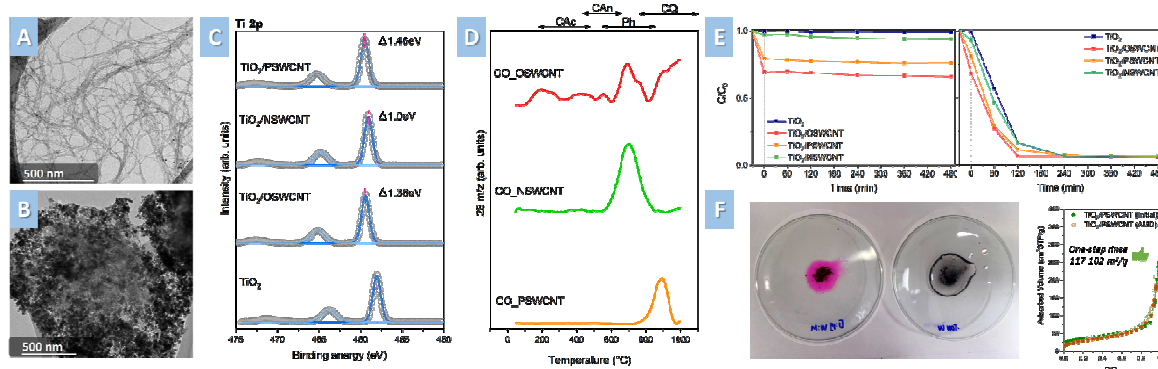


Figure 1 Highlights of the catalyst's physicochemical characterization and photocatalytic performance: A) TEM image of SWCNT material; B) TEM image of TiO₂/OSWCNT composite; C) XPS of all composites and pristine TiO₂ for Ti 2p core level; D) TGA of all composites under inert atmosphere; E) Photocatalytic performance of composites under non/simulated-solar irradiation; F) Desorption experiments of the recovered catalysts after the photocatalytic degradation of Rhodamine-B.

Acknowledgements

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References

- [1] P. Ayala, R. Arenal, M. Rümmele, A. Rubio, T. Pichler, *Carbon* **48** (2010) 575–586.
- [2] T.J. Bandoz, in *Carbon Materials for Catalysis*, John Wiley & Sons, Ltd. (2008) 45–92.
- [3] J.L. Faria, W. Wang, in *Carbon Materials for Catalysis*, John Wiley & Sons, Ltd. (2008) 481–506.



HKUST-1(Cu)@HPCM Composites for Carbon Dioxide Capture

M. Alması^{a*}, A. Badač^b, Ľ. Zauška^a, T. Zelenka^b

^a Department of Inorganic Chemistry, Faculty of Science, Pavol Jozef Safarik University, Moyzesova 11, SK-040 01 Kosice, Slovak Republic

^b Department of Chemistry, Faculty of Science, University of Ostrava, 30. dubna 22, CZ-702 00 Ostrava, Czech Republic

*miroslav.almasi@upjs.sk

Metal-organic frameworks (MOFs) and hierarchically porous carbon monoliths (HPCMs) have emerged as promising materials in CO₂ capture, contributing to efforts to mitigate climate change. MOFs, crystalline materials formed by metal ions/clusters coordinated with organic ligands, boast remarkable porosity and surface area. The porous nature of MOFs facilitates the capture of CO₂ molecules, making them highly efficient adsorbents for this greenhouse gas. Complementing the capabilities of MOFs are HPCMs, 3D carbon structures characterised by a range of pore sizes, including micropores, mesopores, and macropores. HPCMs exhibit a hierarchical pore structure that enhances mass transfer and accessibility of gas molecules to active sites. HPCMs, like MOFs, show promise in CO₂ capture due to their high surface area and customisable properties. Recent research shows a growing interest in integrating MOFs with HPCMs to create hybrid materials. These hybrids leverage the strengths of both components, with MOFs providing exceptional adsorption capacities and hierarchically porous carbon monoliths contributing structural stability. This synergistic approach results in materials that surpass the individual capabilities of MOFs or carbon monoliths, leading to enhanced performance in CO₂ capture applications. This interdisciplinary strategy aims to develop efficient and versatile solutions for carbon capture, addressing the critical need to reduce CO₂ emissions and combat climate change.

The preparation of HKUST-1(Cu)@HPCM composites was realised by three synthetic strategies. In the "dip-coating" method, the HPCM was immersed in a suspension of MOFs in methanol and absorbed into the HPCM structure. A series of experiments were also carried out, which consisted of repeatedly dropping the HKUST-1(Cu) methanol suspension onto the HPCM until the sample adsorbed the suspension - the "dropping" method (see Fig. 1a). However, the results from the adsorption of carbon dioxide at 0 °C did not show an increase in the adsorption capacity of the composite materials compared pristine HPCM. Moreover, the HPCM monoliths cracked and disintegrated after several cycles of methanol suspension addition. SEM/EDX analysis did not show MOF evidence in the centre of the HPCM; it only showed presence on the external surface. Therefore, experiments were performed on the direct synthesis of MOF@HPCM ("in-situ" method), consisting of the immersion (impregnation) of HPCM in the reaction solution for the preparation of HKUST-1(Cu) (see Fig 1b). SEM/EDX and PXRD analysis demonstrated the uniform distribution and presence of HKUST-1(Cu) in the prepared composite. An interesting finding was that with the increasing number of synthesis repetitions of HKUST-1(Cu)@HPCM, the adsorbed capacity of CO₂ increased until it reached an amount comparable to, and in some cases even exceeding, the original HKUST-1(Cu). More detailed information will be presented at the conference, including further analyses of prepared materials.

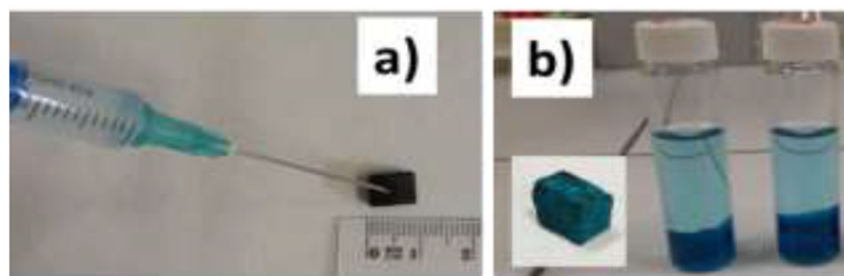


Figure 1a) Preparation of the HKUST-1(Cu)@HPCM composite by the "dropping" method and b) by the "in-situ" method, including a photo of the resulting composite.



This interdisciplinary strategy for preparing composite MOF@HPCM materials aims to develop efficient and versatile carbon capture solutions that address the critical need to reduce CO₂ emissions, combat climate change, and contribute to a sustainable and environmentally conscious future.

Acknowledgements

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MIL-101(Cr) as an Anode Material for Li-ion Batteries

D. Capkova^{a*}, K.M. Ryan^a, M. Almási^b

^a Department of Chemical Sciences and Bernal Institute, University of Limerick, Limerick, V94 T9PX, Ireland

^b Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

*Dominika.Capkova@ul.ie

The main driving force to improve lithium-ion (Li-ion) batteries is the development of mobile electronic devices and electric vehicles. The improvement of anode materials is more urgent than that of cathode materials due to the low specific capacity of graphite. Therefore, scientists have invested a lot of effort in exploring suitable anode materials. Metal-organic frameworks (MOFs) and their derivatives have been found to be applicable in energy storage materials due to their porous and high specific surface area characteristics. However, MOF can be used to encapsulate Si, a promising anode material due to its high theoretical capacity of 4200 mAh g⁻¹. Si suffers from undesired swelling-shrinking and the MOF matrix can effectively mitigate the volume change of Si particles [1, 2].

In this study, MIL-101(Cr) with tetramethylammonium hydroxide (TMAOH) was prepared, carbonized, and used as anode material for Li-ion batteries. The electrode material contained 80% carbonized MIL-101(Cr), 10% Super P and 10% CMC. Coin cell CR2032 was assembled with a glass fibre separator, Li metal foil and 1 M LiPF₆ in EC:DEC as an electrolyte. The cell was preconditioned for one cycle at 50 mA g⁻¹ and then cycled at 100 mA g⁻¹. The initial Coulombic efficiency was ~44% due to the formation of the SEI layer, and the average Coulombic efficiency was around 99%. The specific capacity at 50 mA g⁻¹ was 232 mAh g⁻¹ and 201 for g⁻¹. The material showed stable cycle performance and the capacity retention after 500 at 100 mA g⁻¹ was 76%. The next step in this study is to mix Si nanoparticles with MIL-101(Cr) to significantly improve the electrode material's performance and compare it with a baseline.

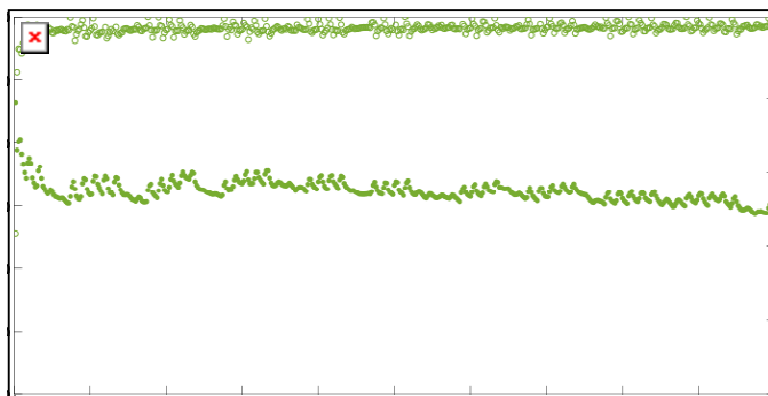


Figure 1 Long-term galvanostatic cycling of anode material with MIL-101(Cr) at 100 mA g⁻¹.

Acknowledgements

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References

- [1] H. Cheng, J.G. Shapter, Y. Li, G. Gao, J. Energy Chem. **57** (2021) 451-468.
- [2] Y. Han, P. Qi, X. Feng, S. Li, X. Fu, H. Li, Y. Chen, J. Zhou, X. Li, B. Wang, ACS Appl. Mater. Interfaces. **7** (2015) 2178-2182.



Characterization of Porosity by Low-Field NMR Relaxometry

E. Kinnertová*, P. Kopčan, V. Slovák

Department of Chemistry, Faculty of Science, University of Ostrava, 30. Dubna 22, 702 00 Ostrava, Czech Republic

*eva.kinnertova@osu.cz

Low-field ^1H -NMR relaxometry can be used for characterization of the structure of porous materials. Since this technique allows observation of samples in a wet state, it provides a suitable alternative or complement to conventional methods (gas sorption, mercury intrusion). The aim of this contribution is to demonstrate the applicability of low-field ^1H -NMR relaxometry for the characterization of wetted carbonaceous materials with different mesoporosity.

Spin-spin relaxation (T_2) of hydrogen nuclei confined in differently mesoporous wetted carbonaceous materials was determined by CPMG pulse sequence using a Minispec mq20 (Bruker).

The experimental relaxation curves were evaluated by non-linear optimization using the Solver tool in Excel and Contin software to obtain estimate of distribution of relaxation times. The observed relaxation times (T_2) and types of present water (hydrogen nuclei) were then assigned to the spaces they fill in the samples. Four types of water were determined for all sufficiently wetted samples related to water in mesopores ($T_2 = 10 - 100$ ms), in macropores or between the particles ($T_2 = 100 - 1500$ ms) and bulk water (above 1500 ms). Some materials showed signals below 10 ms probably related to water in micropores. This study follows on previous one [1] and shifts the implementation of low-field NMR relaxometry for estimation of pore size distribution of porous materials closer to practical applicability.

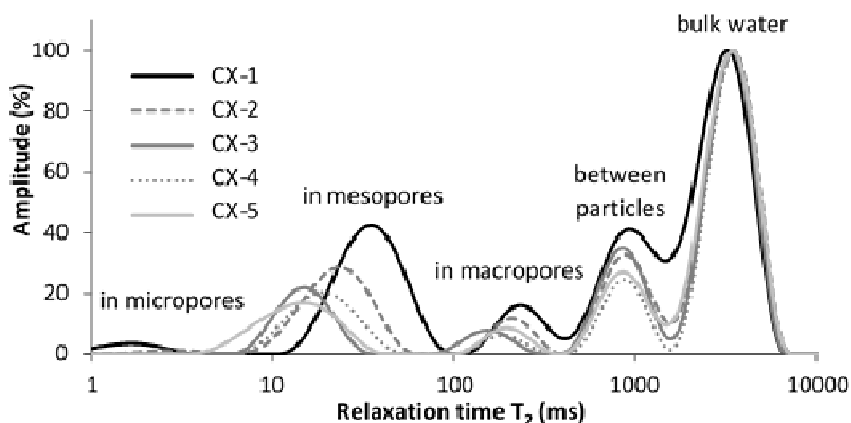


Figure 1 Distribution of T_2 for wet mesoporous carbonaceous samples with the ratio of carbon to water = 1:5 (logarithmic scale on horizontal axis).

Acknowledgements

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References

[1] E. Kinnertova, V. Slovak, T. Zelenka, et al., *Materials* **15** (2022) 9021.



Characterizing Mesoporosity in MOFs: A Thermoporometry Approach

G. Zelenková^{a*}, T. Zelenka^a, M. Almáši^b

^aDepartment of Chemistry, Faculty of Science, University of Ostrava, 30. Dubna 22, 702 00 Ostrava, Czech Republic

^bDepartment of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

*gabriela.zelenkova@osu.cz

Thermoporometry (TPM) is employed to characterize mesoporosity and, to some extent, macroporosity in materials, providing an alternative to the conventional gas physisorption method. This study represents the first use of thermoporometry for evaluating mesoporous metal-organic frameworks (MOFs), which have been developed for various applications. Our research focuses on the original MIL-101(Fe)-NH₂ sample, with the most abundant pore sizes determined to be 3.9 and 5.2 nm by TPM. We also investigated the MIL-101(Fe)-NH₂ variant (MIL-101(Fe)-NH₂-disrupted), which features expanded pores measuring 5.1 and 10 nm. The results indicate that thermoporometry, using water as the immersion liquid, provides results comparable to those from gas (N₂/-196 °C) physisorption (see Figure 1). However, it is important to note that absolute consistency cannot be assumed, due to potential volumetric changes in the material's porosity in the wet state.

This insight into mesoporosity under wet conditions offers valuable additional information for MOF applications in environmental and biomedical fields, such as heavy metal removal and drug delivery, where TPM can provide a more accurate representation of the MOF's functional porosity.

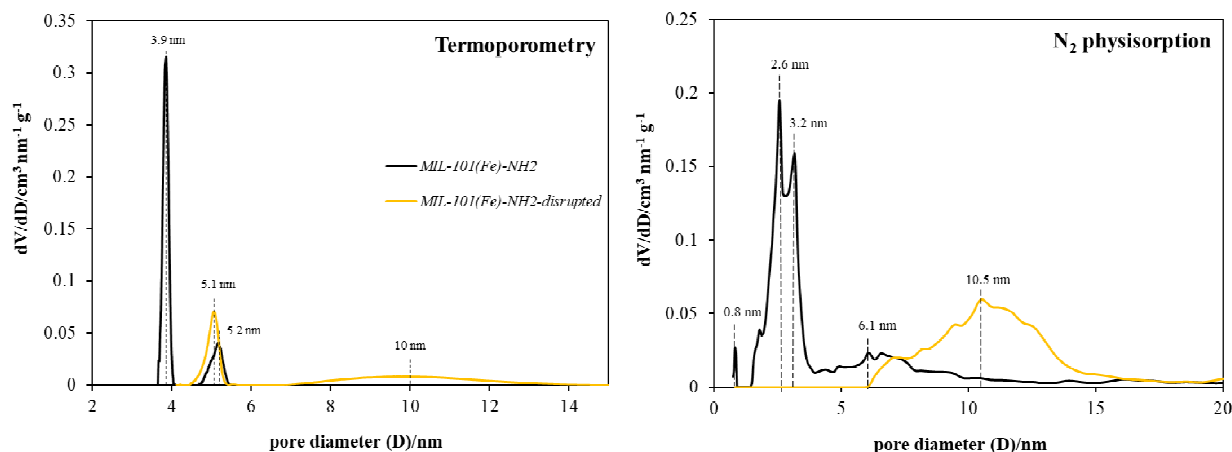


Figure 1 PSD curves obtained by thermoporometry and N₂ physisorption for MIL-101(Fe)-NH₂ and MIL-101(Fe)-NH₂-disrupted samples.

Acknowledgements

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Carbon-based Composite Materials for the Sorption of Cadmium Ions from Aqueous Solutions

J. Holub^a, T. Zelenka^a, M. Almáši^b, A. Badač^a

^a Department of Chemistry, Faculty of Science, University of Ostrava, 30. Dubna 22, 702 00 Ostrava, Czech Republic

^b Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

*Jan.Holub.s01@osu.cz

Composites of metal-organic framework and carbonaceous materials are characterized by high porosity, high specific surface area, high catalytic efficiency (attributed to metal-organic framework) and good conductivity (attributed to carbonaceous materials). Metal-organic framework (MOF) is a crystalline coordination polymer that is composed of an inorganic structure (cation or metal cluster) and a linker (organic ligand), which are joined by a covalent bond. HPCM can be synthesized by combining sol-gel and soft-templating methods, which allow the formation of a hierarchical porous structure. Soft templating is a process in which mesopores are generated within the porous carbon material. This method involves the use of organic compounds, such as Pluronic F127 (a surfactant), that form micelles in the polycondensation mixture. After pyrolysis, these micelles ensure the creation of mesopores. The resulting HPCM possesses a hierarchical pore structure that can be classified into different levels, such as micro-mesoporous, meso-macroporous, micro-macroporous, or even micro-meso-macroporous, depending on the pore distribution[1, 2].

In this work, we focused on preparing composite materials made of metal-organic frameworks (MOFs) and hierarchically porous carbon monoliths (HPCM). The synthesis was performed *in situ*, meaning that MOF crystals were directly formed within the pores of HPCM during the preparation process. Firstly, a solution for MOF synthesis was prepared, into which HPCM monoliths were immersed. The reaction mixture was then heated to a specific temperature (80-85°C) based on the chosen MOF (HKUST-1, MIL-101, or MOF-76). The synthesis condition was optimized by adjusting the concentration of the precursor solution. And the adsorbed amounts of Cd(II) for the composites were found to be 11.5 mg/g for HPCM-OH+HKUST-1, 10.9 mg/g for HPCM-OH+MIL-101 and 11.1 mg/g for HPCM-OH+MOF-76.

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References:

- [1] D. Qian, L. Cheng, H. Guang-Ping, L. Wen-Cui, L. An-Hui, ACS Appl. Mater. Interfaces **4** (2014) 6125-6132.
- [2] P. Bulavová, J. Parmentier, V. Slovák, Microp. Mesop. Mater. **272** (2018) 155-165.



Surface-modified Hierarchically Porous Carbon Monolith for Carbon Dioxide Adsorption

L. Kořená^{a*}, T. Zelenka^a, M. Almáši^b, G. Zelenková^a, K. Koval^c, E. Kinnertová^a, V. Slovák^a,
J. Silvestre-Albero^d, D. Římnáčová^e

^aDepartment of Chemistry, Faculty of Science, University of Ostrava, 30. Dubna 22, 702 00 Ostrava, Czech Republic

^bDepartment of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

^cInstitute of Materials Research, Slovak Academy of Sciences, Watsonova 47, 04001 Košice, Slovakia

^dLaboratorio de Materiales Avanzados, Departamento de Química Inorgánica-Instituto Universitario de Materiales, Universidad de Alicante, San Vicente del Raspeig E-03690, Spain

^eInstitute of Rock Structure and Mechanics, Czech Academy of Sciences, V Holesovickach 41, 182 09 Prague 8, Czech Republic

*lucie.korena@osu.cz

Global warming is, generally, attributed to an increasing amount of greenhouse gases in the atmosphere. The probably most important greenhouse gas is carbon dioxide. The possible ways of reducing the amount of carbon dioxide in the atmosphere include its adsorption on a suitable porous material.

Such suitable porous material with the potential to be successfully used for the carbon dioxide adsorption is the hierarchically porous carbon monolith (HPCM) [1]. To study the effect of surface chemistry on the carbon dioxide adsorption, the surface of HPCM was modified with nitrogen functional groups. The nitrogen functional groups were introduced onto HPCM surface using three different treatments: nitration-reduction treatment, treatment with melamine, and oxidation-amination treatment. The original and prepared surface-modified HPCMs were then characterized in detail by elemental analysis, SEM, XPS, and by nitrogen sorption at 77 K and then, finally, subjected to carbon dioxide sorption at 273 K.

The original HPCM was found out to adsorb approximately 1.8 mmol CO₂/g, while the surface modified HPCMs were found out to adsorb 1.2-1.6 mmol CO₂/g depending on the surface modification treatment.

Acknowledgements

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References

[1] P. Bulavova, J. Parmentier, V. Slovak, *Microp. Mesop. Mater.* **272** (2018) 155-165.



Preparation and Characterization of MMM-MOF Composite Materials

L. Zelená^{a,b*}, M. Almáší^a, T. Zelenka^b, J. Bednarčík^c, P. Diko^c

^a Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

^b Department of Chemistry, Faculty of Science, University of Ostrava, 30. dubna 22, Ostrava, CZ-702 00 Czech Republic

^c Institute of Experimental Physics, Slovak Academy of Sciences, Watsonova 47, SK-040 01 Košice, Slovak Republic

*lucie.zelena@student.upjs.sk

The hierarchically porous carbonaceous monolith (MMM) is known for its high porosity, which is characterized by an interconnected network of micro-, meso- and macropores. This material also offers large surface area and volume, thermal stability, easy surface functionalization and biocompatibility. Due to these exceptional properties, it finds diverse applications in catalysis, gas storage and separation, drug delivery systems and environmental remediation, including wastewater treatment. [1]

Another highly regarded class of porous materials is MOFs, or Metal-Organic Frameworks. These organometallic compounds consist of metal ions or clusters coordinated with organic ligands, forming a porous network. MOFs have gained significant attention in recent years due to their large surface area, tunability (allowing for changes in chemical properties by modifying the metal or organic ligand), kinetic and thermodynamic stability, low cytotoxicity, and ease of surface functionalization. These features make them ideal for a wide range of applications, including wastewater treatment, environmental biosystems, drug delivery, gas storage, hydrogen energy, and more. [2]

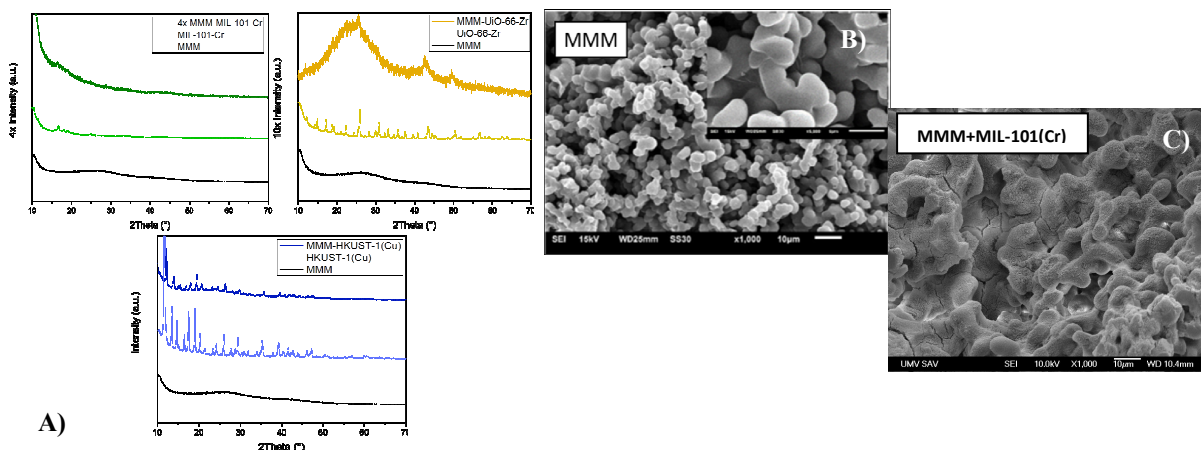


Figure 1 A) XRD images of MMM, MOFs (HKUST-1(Cu);UiO-66(Zr);MIL-101(Cr)) and their composites, B) SEM images of MMM and C) SEM images of MMM+MIL-101(Cr).

This work focuses on the synthesis of MMM-MOF composite materials. These composite materials were prepared by *in-situ* method, which means that MOF crystals formed directly within the MMM pores during the preparation of the material. The already prepared MMM cubes were introduced into the prepared solution used for the synthesis of MOF material (HKUST-1(Cu), UiO-66(Zr) and MIL-101(Cr)) and the mixture was heated to the desired temperature. The reactions were optimized by adjusting variables such as time, initial solution concentration, and the number of MMM monolith cubes. The prepared composite materials were examined by X-ray diffraction, which confirmed the presence of the desired MOFs as shown in Figure 1A). Also, the presence of MOFs as a layer covering the carbon surface was depicted using SEM analysis (Fig. 1C)). These results confirm the successful preparation of composite materials. The integration of these two porous materials has the potential to create highly porous structures that could effectively address problems such as the treatment of



pollutants from wastewater, the capture of various gases or could be used, for example, as drug carriers to contribute to the treatment of various diseases.

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[1] P. Bulavová, J. Parmentier, V. Slovák, *Microp. Mesop. Mater.* **272** (2017) 155-165.

[2] L. Zhang, Q. Zheng, Z. Zhang, H. Li, X. Liu, J. Sun, R. Wang, *Int. J. Mol. Sci.* **24** (2023) 2145.



Synthesis and Characterization of Palladium-doped HPCM@Pd Composites for Hydrogen Storage

J. Vyhřídálová^a, L. Zauška^{b*}, T. Zelenka^a, M. Almáši^b

^aDepartment of Chemistry, Faculty of Science, University of Ostrava, 30. dubna 22, CZ-702 00 Ostrava, Czech Republic

^bDepartment of Inorganic Chemistry, Faculty of Science, Pavol Jozef Safarik University, Moyzesova 11, 040 01 Kosice, Slovak Republic

*lubos.zauska@student.upjs.sk

The quest for sustainable and efficient energy storage solutions has driven research towards the development of advanced materials with enhanced hydrogen storage capacities. In this context, Hierarchical Porous Carbon Materials (HPCMs) have emerged as promising scaffolds due to their extensive surface areas, tunable pore structures, and exceptional chemical stability. However, the hydrogen storage capabilities of HPCMs can be significantly augmented by incorporating metal nanoparticles that facilitate spillover and adsorption phenomena. This study introduces a novel synthesis route for Palladium-functionalized Hierarchical Porous Carbon Materials (HPCM@Pd), aiming to exploit the synergistic effects between the porous carbon framework and palladium nanoparticles for improved hydrogen storage performance. Leveraging the unique properties of palladium, including its high hydrogen absorption capacity and catalytic activity, we hypothesize that the HPCM@Pd composite will exhibit superior hydrogen storage metrics compared to its counterparts.

HPCM@Pd composites were synthesized using varied methodologies to ascertain the most effective approach for enhancing hydrogen storage. The initial method involved the impregnation of pre-synthesized Pd nanoparticles into pristine HPCM material, followed by a comparison with the grafted surface of HPCM with (3-mercaptopropyl)trimethoxysilane and thioglycolic acid. The second method entailed the *in situ* formation of Pd nanoparticles within both the unmodified and surface-modified HPCM frameworks. Finally, the third approach integrated Pd nanoparticles into the sol-gel process during the fabrication of the HPCM precursor, specifically within a resorcinol-formaldehyde gel (R-F gel, see Fig. 1) matrix. These methodologies were meticulously compared to determine their impact on the material's structure and, consequently, on its hydrogen storage capabilities, aiming to identify the most efficient synthesis route for optimizing the performance of HPCM@Pd composites.

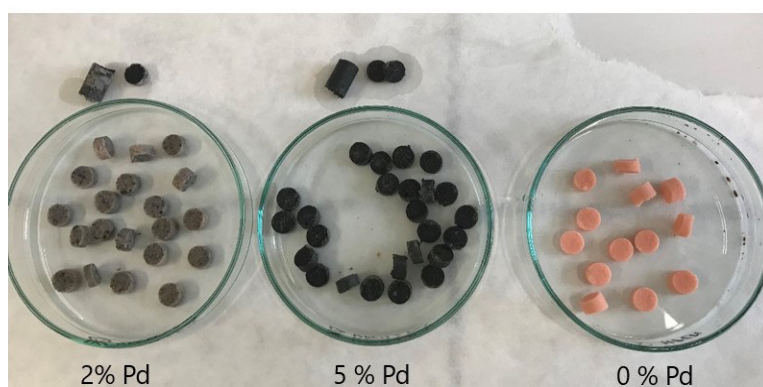


Figure 1 Different amount of Pd nanoparticles in R-F gel.

Hydrogen storage is crucial for fuel applications due to its potential for high energy density, but the challenge lies in developing safe, efficient, and cost-effective storage solutions. These methods were evaluated for their effect on the composite's structure and hydrogen storage efficiency, aiming to pinpoint the most effective synthesis approach for HPCM@Pd composites.



Acknowledgements

This work was supported by APVV SK-CZ-RD-21-0068 and LUASK22049 (INTER-EXCELLENCE II, MŠMT) and NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project No. 09I03-03-V03-00034.



Tuning Porosity in Carbon Monoliths for CO₂ Capture and H₂ Storage

M.P. Chavhan*

Department of Chemistry, Faculty of Science, University of Ostrava, 30. Dubna 22, 702 00 Ostrava, Czech Republic

*Madhav.Chavhan@osu.cz

Carbon nanostructures in forms such as powders, films, fibres, or monoliths are highly promising for applications such as energy storage, catalysis, and adsorption. Monoliths are particularly advantageous as a result of their ease of handling, low attrition, and nontoxicity compared to powders. However, tuning porosity in monoliths is challenging to prevent slow diffusion and pressure drop issues. A pore hierarchy is desirable, with meso-macropores enabling fast diffusion, and micropores providing most of the surface area for active sites.

In this study, the sol-gel polycondensation route of polymer precursors, followed by carbonization, is used to obtain carbon monoliths. The tuning of sol-gel chemistry parameters along with the soft templating approach using pluronics F127 surfactant was utilized to induce mesoporosity [1], and the high temperature of carbonization along with CO₂ exposure was followed further for micropore activation [2]. In addition, the incorporation of different proportions of graphene oxide into the polymeric sol was carried out to induce highly crosslinked polymerized gel networks, which on carbonization and post-activation lead to the additional development of micropore features. With the above-mentioned modifications, the resulting carbon monoliths samples show promise for enhanced adsorption capacities for both CO₂ and H₂ gas probe molecules. The maximum capacities for CO₂ and H₂ adsorption were found to be 5 mmol g⁻¹ (at 0 °C and 101 kPa) and 12.8 mmol g⁻¹ (at – 196 °C and 101 kPa), respectively.

References

- [1] M.P. Chavhan, M. Musielak, V. Slovák, *Microp. Mesop. Mater.* **366** (2024) 112919.
- [2] M.P. Chavhan, S. Ganguly, *J. Sol-Gel Sci. Technol.* **88** (2018) 395–406.



Fe₂O₃/Cr₂O₃ Supported on Activated Carbon for H₂S Removal at Room Temperature

M. Abid*, Ó.J. Amorós, J.S. Albero

Advanced Materials Lab, Inorganic Chemistry Department, University of Alicante, Spain

*abidmeriem095@gmail.com

Hydrogen sulfide (H₂S) is a pollutant of high toxicity and corrosivity that inevitably is present in the atmosphere as a result of natural and anthropogenic processes. Its sources include anaerobic digestion, geothermal or volcano eruptions, and oil refineries. It is extremely needed to develop an efficient technology for capturing and removing gaseous pollutants to reduce their environmental impact. A deeper hydrogen sulfide removal is necessary due to actual environmental regulations. Despite the tremendous advancement in H₂S adsorption technology over the years, efforts in designing new materials have been an ever-growing interest for enhancing breakthrough time with better adsorption and/or catalytic capacity. In particular, Extensive studies have been reported on the development of new low-cost, highly reactive, and easily synthesized adsorbents, such as zeolite, metal oxides (or hydroxide), membrane, and activated carbon [1]. The desulfurization onto carbon materials has been pointed out as an attractive technology in many studies aiming at evaluating different catalysts with high potential for that purpose. Based on these premises, the main goal of the present study is the evaluation of the H₂S removal performance using commercial carbon modified with two metals (iron and chromium) as an adsorbent. These results anticipate that metal oxide based carbon nanoparticles exhibit a promising performance for the H₂S removal up to 387 mg/g.

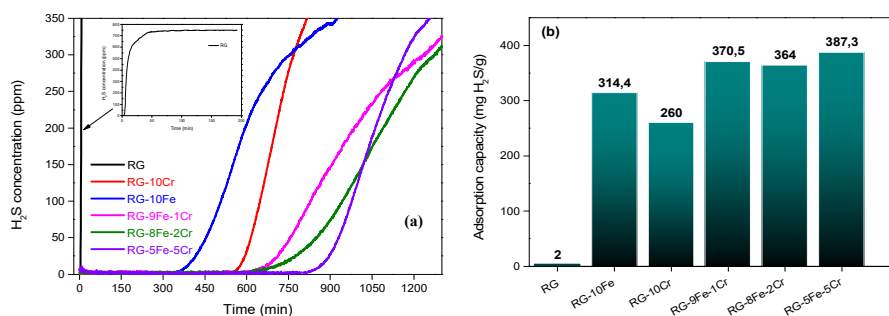


Figure 1 The breakthrough curves (a) and H₂S removal capacity (b) of the prepared adsorbents.

Acknowledgements

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References

[1] T.J. Bandoz, J. Colloid Interf. Sci. **246** (2002) 1–20.



Novel HKUST-1@HPCM Composite for Removal of Pesticide Dicofol from Water

M. Želinská^{a*}, L. Zauška^a, T. Zelenka^b, M. Almáši^a

^aDepartment of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzešova 11, 040 01 Košice, Slovak Republic

^bDepartment of Chemistry, Faculty of Science, University of Ostrava, 30. Dubna 22, 702 00 Ostrava, Czech Republic

*milica.fabisikova@upjs.sk

Pesticides represent a wide group of substances used to control and prevent different pests. The major class – the organochlorines (OCPs) are organic molecules containing chlorine atoms characterized by low polarity and solubility in water, but high solubility in fats. This characteristic contributes to their persistence in the environment and the food chain, which poses significant threats to the ecosystem and, ultimately, human health. Dicofol, a typical representative of organochlorine pesticides, has been extensively used in past decades for effective prevention and control of mites pests. It is a broad-spectrum contact, non-systemic miticide and acaricide used mainly to protect cotton, variety of fruit and vegetables. Dicofol has been extensively employed in numerous countries across the world, however due to concerns about its toxicity and persistency, dicofol has been already prohibited in all developed countries. Dicofol has low solubility in water, can bind strongly to soil and can be transported via rivers to the open sea and then accumulate in sediments. It can also be a subject of long range transport via air. Dicofol has a high bioaccumulation and biomagnification potential in both air-breathing organisms and aquatic organisms. Residues of this pesticide have been found in different species like mammals, reptiles/amphibians, fish, birds and also in humans and breast milk. Dicofol has been found to have adverse effects in endocrine organs, reproductive development, hormonal imbalances and neurotoxicity. The presence of dicofol in human bodies is likely to have negative impacts on human health. Dicofol is classified as acutely toxic if swallowed or inhaled, causing skin irritation and may lead to an allergic skin reaction. Additionally, it has been found to damage red blood cells and lymphocytes and has been classified as a possible human carcinogen.[1,2,3]

Considering environmental and toxicological risk of dicofol, there is a need for effective removal techniques. Up to now several methods have been developed to degrade or remove dicofol like oxidation, biological degradation, electrochemical treatment, sonochemical degradation, photochemical degradation and adsorption. Adsorption is widely recognized as one of the most effective, low energy consumption, and cost-efficient method for removal different pollutants. In general, porous materials with high surface areas, such as activated carbons, zeolites, mesoporous silica, and metal-organic frameworks (MOFs), are considered superior for pesticide adsorption. MOFs, or Metal-Organic Frameworks, are a class of crystalline compounds that consist of metal ions or clusters coordinated to organic linkers. MOFs are known for their extraordinarily high surface areas, tunable pore size, and adjustable internal surface properties.[4]

Presented study focuses on the preparation and characterization of new composite material consisting of Hierarchically Porous Carbon Monolith (HPCM) and Metal-Organic Framework and its use as effective adsorbents for the removal of pesticide dicofol from water. Combining the properties of both components can result in increased adsorption capacity, selectivity, and improved stability. Here, we report the synthesis of novel composite prepared *in situ* from HPMC and HKUST-1, which properties and adsorption potential under different conditions will be investigated.

Acknowledgements

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References

- [1] WHO (1996): International Programme on Chemical Safety, Dicofol, WHO/FAO Data Sheets on Pesticides No. 81 World Health Organization. Geneva, July 1996.
- [2] UNEP (2021). Guidance on preparing inventories of dicofol. Secretariat of the Basel, Rotterdam and Stockholm conventions, United Nations Environment Programme, Geneva. Protection Council.



[3] A. Thiel, S. Guth, S. Böhm, G. Eisenbrand, *Toxicology* **282** (2011) 88-93.

[4] G.P. Pandey, A.K. Singh, L. Deshmukh, A. Asthana, *Inor. Metal-Org. Nano-Met. Chem.* **45** (2015) 1199-1205.



UiO-66-NH₂@HPCM Composites for Carbon Dioxide Storage

M. Almäši^{a*}, L. Kořenáb, T. Zelenka^a, G. Zelenková^b, E. Kinnertová^b

^a Department of Inorganic Chemistry, Faculty of Science, Pavol Jozef Safarik University, Moyzesova 11, 040 01 Kosice, Slovak Republic

^b Department of Chemistry, Faculty of Science, University of Ostrava, 30. Dubna 22, 702 00 Ostrava, Czech Republic

*miroslav.almasi@upjs.sk

Hierarchically porous carbon monoliths (HPCM) with metal-organic framework (MOF) composites fuse the structured porosity and high surface area of both materials and combine micro-, meso-, and macropores, enhancing accessibility and transport properties. This synergy creates materials with unique properties that are ideal for a variety of applications, e.g., gas storage/separation, energy storage and conversion, heterogeneous catalysis, and environmental applications.

The synthesis of composite materials containing microporous MOF (UiO-66-NH₂) in combination with HPCM doped with different nitrogen functional groups in order to enhance their CO₂ adsorption capacity was studied. Adsorption of CO₂ on amine groups is a well-researched area due to its importance in carbon capture and storage (CCS) technologies. Amine-based adsorbents are highly effective at capturing CO₂ from gas streams, particularly in low-concentration environments such as flue gases from power plants and industrial companies. For these reasons, UiO-66-NH₂, which contains an amine group in the linker, was chosen, and the HPCM surface was post-synthetically modified/doped with amine groups or nitro groups with different amounts, respectively. The prepared materials were characterized by elemental analysis, infrared and X-ray photoelectron spectroscopy, scanning electron microscopy, powder diffraction analysis, nitrogen adsorption/desorption and thermal analysis. The MOF content in the resulting composite was calculated based on the weight loss changes between the HPCM and the composites using thermal analysis, with the amounts ranging from 15-30 wt. %. The results of CO₂ adsorption at 0 °C and pressure up to 1 atm showed that the presence of nitrogen functional groups on the HPCM surface and the presence of MOFs in the UiO-66-NH₂@HPCM composite increased the adsorption capacity of HPCM by 3.5-5 times more.

Acknowledgements

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Two Types of Mesoporous HKUST-1 Materials as Heterogeneous Catalysts

N. Vargová^{a*}, N. Király^a, R. Serbin^b, M. Almáši^a

^a Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science UPJS, Moyzesova 11, 041 54 Kosice

^b Department of Analytical Chemistry, Institute of Chemistry, Faculty of Science UPJS, Moyzesova 11, 041 54 Kosice

*nikola.vargova2@student.upjs.sk

Metal-organic frameworks (MOFs) are a class of crystalline materials composed of metal ions or clusters coordinated to organic ligands, forming a porous, three-dimensional networks. These materials are known for their high surface area, tunable pore sizes, and structural rigidity.[1] MOFs exhibit remarkable versatility, with applications in gas storage and separation, catalysis, drug delivery, and sensing. Metal-organic frameworks have gained significant attention in heterogeneous catalysis due to their highly tunable structures, large surface areas, and well-defined porous networks. The ability to incorporate a variety of metal nodes and organic linkers allows for precise control over the active sites within the framework, enhancing catalytic efficiency and selectivity. These features make MOFs particularly effective in facilitating reactions such as oxidation, hydrogenation, and condensation, where the accessibility of reactants to catalytic sites is critical.[2]

In the presented study, we focused on the synthesis and investigation of the catalytic properties of mesoporous materials HKUST-1(A) and HKUST-1(B). The synthesis was conducted using a solvothermal method involving trimesic acid (H₃BTC), Cu(NO₃)₂, and dimethylformamide (DMF). Cetyltrimethylammonium bromide (CTAB) and citric acid were subsequently added to the mixture. The reaction mixture was sonicated for 10 minutes and then heated at 75 °C for 24 hours. The resulting blue crystals were filtered and washed with DMF. Surfactant removal was performed in several steps. Initially, a 1 M solution of NH₄NO₃ in EtOH:H₂O (1:2) was added, and the reaction mixture was heated at 60 °C for 24 hours. After 24 hours, the solution was decanted and replaced with EtOH:H₂O (1:2), and the mixture was stirred at room temperature for another 24 hours. The final step involved washing the material with methanol using a Soxhlet extractor for 3 days. The prepared materials were characterized by infrared spectroscopy, thermal analysis, and sorption measurements, which revealed that HKUST-1(A) contains both micro/mesopores, while HKUST-1(B) contains only mesopores. The BET surface area reaches 1534 m²·g⁻¹ and 1709 m²·g⁻¹, respectively for HKUST-1(A) and HKUST-1(B). In addition to the mesopores with a diameter of 19.6 nm, the sample contains micropores with a diameter of 0.86 nm, which is in line with the micropore diameter (0.86 nm) estimated from crystallographic data of Cu₃(BTC)₂. These results demonstrate that, by using a cooperative template, mesoporous MOFs with hierarchical structure have been successfully fabricated, in which mesopore walls consist of microporous frameworks. The catalytic properties of these materials were initially examined using a model reaction, specifically the Knoevenagel condensation between benzaldehyde (**PhCHO**) and malononitrile. In this reaction, we studied the effects of solvent (toluene, acetonitrile, xylene), temperature (60 °C, 80 °C, 100 °C), and catalyst amount (25 mg, 50 mg). The results indicated that the optimal conditions were toluene as the solvent, a temperature of 80 °C, and a catalyst amount of 50 mg. Under these conditions, the influence of halogen and nitro substituents in the *ortho*- (2-fluorobenzaldehyde **2-F**, 2-chlorobenzaldehyde **2-Cl**, 2-bromobenzaldehyde **2-Br**, 2-nitrobenzaldehyde **2-NO₂**) and *para*- (4-fluorobenzaldehyde **4-F**, 4-chlorobenzaldehyde **4-Cl**, 4-bromobenzaldehyde **4-Br**, 4-nitrobenzaldehyde **4-NO₂**) positions relative to the carbonyl group was investigated. In both cases, HKUST-1(B) demonstrated superior performance. Among the *ortho*-substituted compounds, 2-nitrobenzaldehyde achieved the highest conversion of 96%. For the *para*-substituted compounds, 4-chlorobenzaldehyde achieved the highest conversion of 97%. Regarding HKUST-1(A), the highest conversion for *ortho*-substituents was 84% with 2-fluorobenzaldehyde, while the highest conversion for *para*-substituents was 91% with 4-chlorobenzaldehyde.

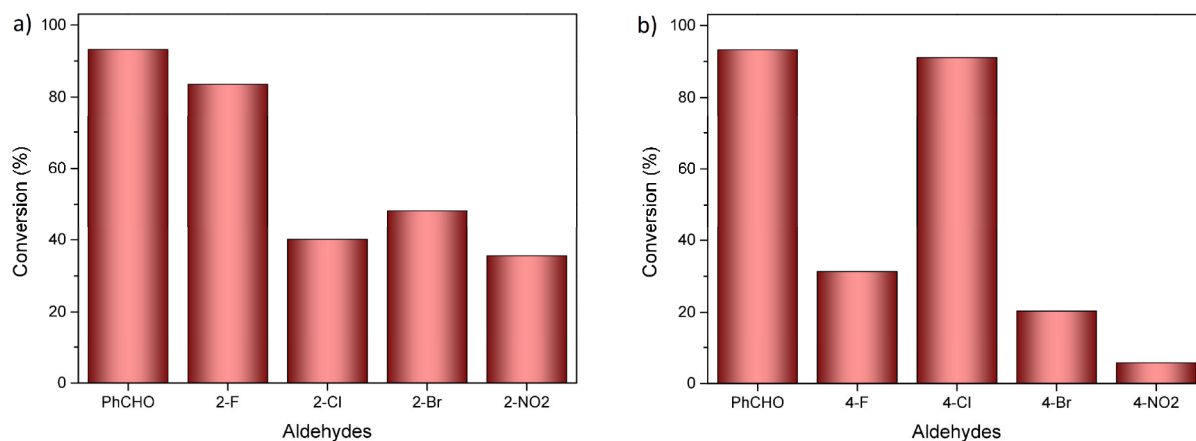


Figure 1 Comparison of reaction conversions catalyzed by HKUST-1(A) using a) ortho and b) para substituents.

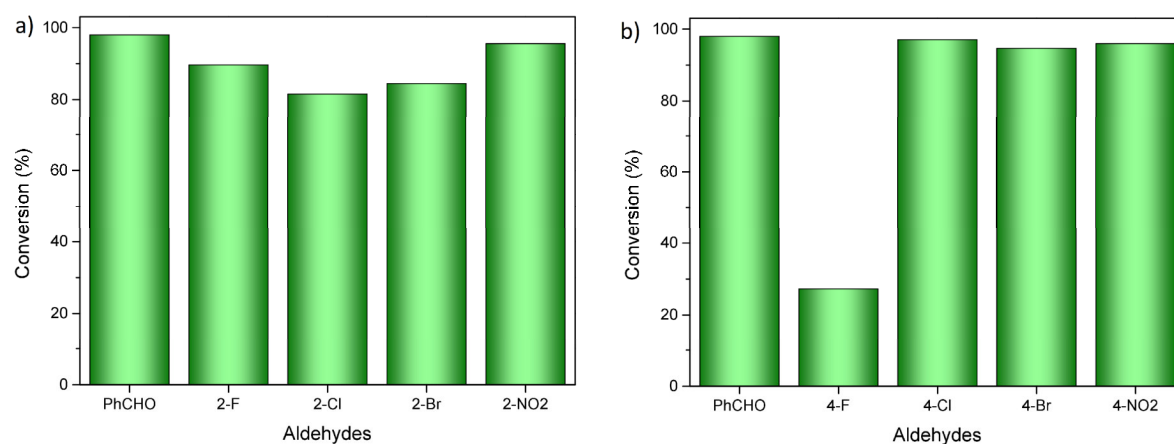


Figure 2 Comparison of reaction conversions catalyzed by HKUST-1(B) using a) ortho and b) para substituents.

Acknowledgements

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References

- [1] C. Xu, R. Fang, R. Luque, L. Chen, Y. Li, *Coord. Chem. Rev.* **388** (2019) 268-292.
- [2] K. Van Beurden, S. de Koning, D. Molendijk, J. van Schijndel, *Green Chem. Lett. Rev.* **13** (2020) 349-364.



Porous Coordination Network PCN-160 as a Heterogeneous Catalyst

N. Vargová^{a*}, N. Király^a, R. Serbin^b, M. Almáši^a

^a Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science UPJS, Moyzesova 11, 041 54 Kosice

^b Department of Analytical Chemistry, Institute of Chemistry, Faculty of Science UPJS, Moyzesova 11, 041 54 Kosice

*nikola.vargova2@student.upjs.sk

Metal-organic frameworks (MOFs) represent a rapidly emerging class of porous materials, characterized by the coordination of organic ligands with metal ions or metal clusters. These materials are distinguished by their high specific surface area, extensive and tunable porosity, rigid frameworks, adjustable biocompatibility, facile synthesis, and potential for post-synthetic modification.[1] Owing to these properties, MOFs find wide application in areas such as gas separation and storage, removal of heavy metals and environmental pollutants, and they are also employed as components in magnetic and electronic devices, drug delivery carriers, and heterogeneous catalysts.[2]

In this study, we focused on the synthesis, characterization, and investigation of the catalytic properties of the material PCN-160 $\{[\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{ADB})_6]\cdot\text{DMF}\}_n$. The coordination polymer was synthesized under solvothermal conditions in the presence of DMF and CF_3COOH at 120 °C. The material was subsequently subjected to elemental analysis, infrared spectroscopy, and PXRD analysis, which confirmed the coordination of the organic ligand H_2ADB in the form of twelve ADB^{2-} anions bridging zirconium clusters. The catalytic properties were studied using the Knoevenagel condensation reaction between benzaldehyde and malononitrile to produce benzylidenemalononitrile. The reaction progress was monitored using GC analysis, and the product was identified via IR spectroscopy and ^1H NMR spectroscopy. The initial step involved the removal of DMF molecules from the material's cavities and subsequent activation of the material. Next, the influence of different solvents on the catalytic reaction was studied, utilizing five solvents: 1,4-dioxane, acetonitrile, tetrahydrofuran, xylene, and toluene. Based on the results obtained, the effect of temperature was further examined at three temperatures: 60 °C, 80 °C, and 100 °C. The findings indicate that the most favorable conditions are a temperature of 100 °C and the presence of toluene as the solvent. Finally, the catalytic properties of PCN-160 were compared with those of other microporous and mesoporous materials. The highest conversion, 96%, was achieved by MIL-101(Cr), attributed to its mesoporous nature. HKUST-1 followed with a conversion of 90%, which can be ascribed to its large surface area. Subsequently, PCN-160 achieved a conversion of 49%. The lowest conversions were observed with the materials PbMTA and DUT-28, with conversion rates of 19% and 13%, respectively.

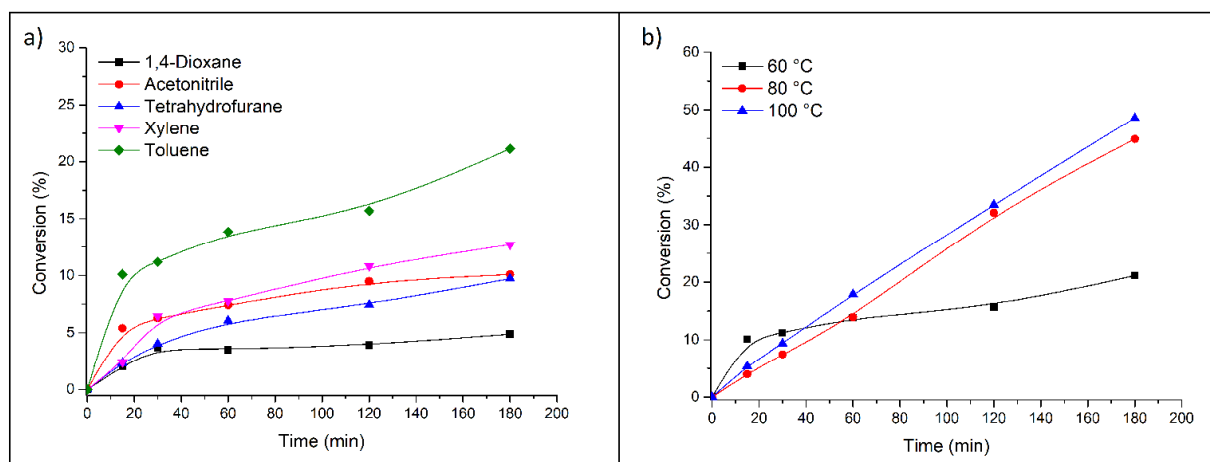


Figure 1 The influence of a) solvent, b) temperature on the catalytic reaction process.

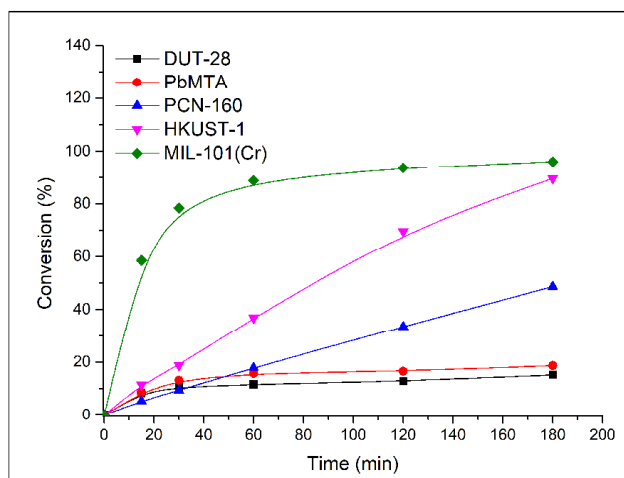


Figure 2 A comparison of the catalytic properties of PCN-160 with other MOF materials.

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References

- [1] C. Xu, R. Fang, R. Luque, L. Chen, Y. Li, *Coord. Chem. Rev.* **388** (2019) 268-292.
- [2] L. Jiao, J.Y.R Seow, W.S. Skinner, Z.U. Wang, H.L. Jiang, *Mater. Today* **27** (2018) 43-68.



The Impact of Hand Grinding and Mechanical Activation on the Stability, Particle Size, Textural Properties, and Carbon Dioxide Adsorption of HKUST-1 and MOF-76.

N. Király^{a*}, T. Zelenka^b, A. Királyová^a, L. Zauška^a, M. Želinská^a, M. Almáši^a

^aDepartment of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

^bDepartment of Chemistry, Faculty of Science, University of Ostrava, 30. Dubna 22, 702 00 Ostrava, Czech Republic

*nikolas.kiraly@upjs.sk

Metal–organic frameworks (MOFs) are a versatile class of porous materials characterized by their exceptional structural diversity, tunability, porosity, and surface area. These frameworks are composed of metal nodes or clusters connected by organic linkers, creating a three-dimensional structure with well-defined and uniformly distributed pores. The synthesis of MOFs offers a high degree of customization, allowing precise control over properties such as pore size, surface area, and functional groups. Due to their remarkable characteristics, MOFs have garnered significant interest across various scientific fields. Their extensive surface area and pore volume make them ideal candidates for gas capture, storage, and separation, including the sequestration of environmentally harmful gases and organic pollutants, as well as the selective adsorption of specific molecules. Moreover, the tunable properties of MOFs facilitate the design of materials for applications in heterogeneous catalysis, where the pore environment and metal sites can be engineered to enhance catalytic activity and selectivity [1–4].

This study investigates the impact of mechanical treatment on two metal–organic frameworks (MOFs), HKUST-1 and MOF-76, by employing various milling techniques to evaluate their effects on stability, porosity, and CO₂ adsorption capacity. The research compares the influence of different mechanical grinding methods, including high-energy ball milling and hand grinding, on these MOFs. The effect of parameters such as milling time, speed, and ball size during high-energy ball milling was systematically assessed using a 3³ Taguchi orthogonal array as part of a Design of Experiments (DoE) approach. Results demonstrate that hand milling significantly enhances the CO₂ adsorption capacity of HKUST-1, with an increase from 25.70 wt.% (5.84 mmol g⁻¹) to 41.37 wt.% (9.40 mmol g⁻¹), representing a 38% improvement. Conversely, high-energy ball milling was found to reduce the CO₂ adsorption capacity. MOF-76 exhibited resistance to hand grinding, maintaining properties close to the original sample, and the hand grinding method was shown to be reproducible. These findings underline the nuanced effects of mechanical milling on MOF materials and highlight the need for careful selection of processing techniques to optimize stability, porosity, and performance in CO₂ capture and storage applications. Additionally, the study underscores the importance of optimizing milling conditions to tailor MOF properties for various applications, particularly in gas adsorption and separation processes, and suggests avenues for further research in MOF synthesis and engineering.

Acknowledgements

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References

- [1] M. Ding, X. Cai, H. Jiang, *Chem. Sci.* **10** (2019) 10209–10230.
- [2] V. F. Yusuf, N. I. Malek, S. K. Kailasa, *ACS Omega* **7** (2022) 44507–44531.
- [3] W. Fan, X. Zhang, Z. Kang, X. Liu, D. Sun, *Coord. Chem. Rev.* **443** (2021).
- [4] H. Li. *EnergyChem* **1** (2019) 100006.



Soft-templated Carbon Monoliths with Hierarchical Porosity for Adsorption from Liquids

P. Bulavová^{a*}, J. Parmentier^b, V. Slovák^a

^a Department of Chemistry, Faculty of Science, University of Ostrava, 30. dubna 22, 702 00 Ostrava, Czech Republic

^b Institute of Material Sciences of Mulhouse (IS2M), Université de Haute-Alsace, France

* petra.bulavova@osu.cz

Carbon monoliths with controlled multi-scale porosity were easily prepared by a combination of sol-gel and soft-templating methods. Compare to other synthesis of porous carbon monoliths, there were no need of prepolymerisation step of the resin, macrophase separation agent such as polyethyleneglycol, cosurfactant, peculiar drying conditions or hydrothermal step. Appropriate synthesis conditions succeeded, with only addition of ethanol/water mixture and Pluronic F127 as a template, to yield porous carbon monolith materials with controlled porosities. Thus, during the polymerisation step, both macroscopic phase separation leading to macropores together with the soft-template mechanism which tailor the mesoporosity takes place (Fig. 1).

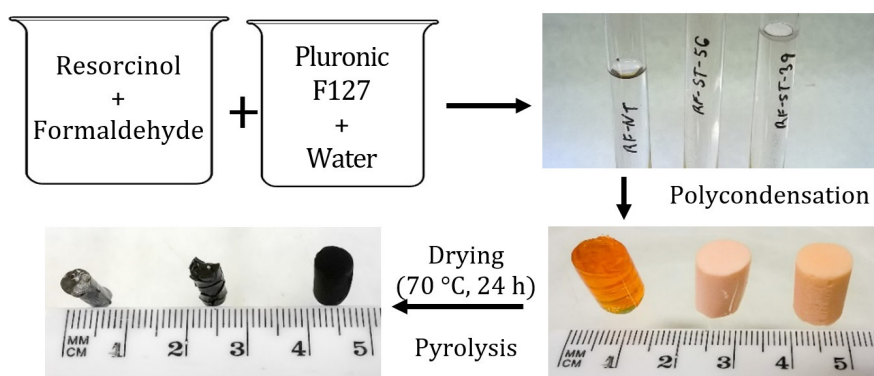


Figure 1 Preparation scheme of carbon monoliths.

Model materials with different porosities were elaborated: only microporous (without template), micro-mesoporous (with soft template: resorcinol ratio 2:1) and micro-meso-macroporous (for soft template: resorcinol ratio 1:1) samples. This panel of model porous materials allowed to evidence and quantify the significance of mesopores and macropores for adsorption kinetics of materials having micropores. The ability of CO₂ to diffuse (at 30 °C) through the ultramicroporous network was not affected by presence of meso- and macropores. On the other hand, mesopores were found to be crucial for successful diffusion of N₂ (at -196 °C) into ultramicropore network of carbon monolith.

For adsorption from liquid media, both mesopores and macropores present in the templated samples were found to be of primary significance for fast kinetics of adsorption. The only presence of ultramicropores did not enable the diffusion of neither phenol nor methylene blue to the active sites. At the opposite, the presence of mesopores allowed the diffusion of both species from mesopores adsorption sites (micropores/smaller mesopores). Diffusion was further improved by the presence of extra macropores. These results were proved by calculation of the effective diffusion parameter based on the Crank's intraparticle diffusion model.

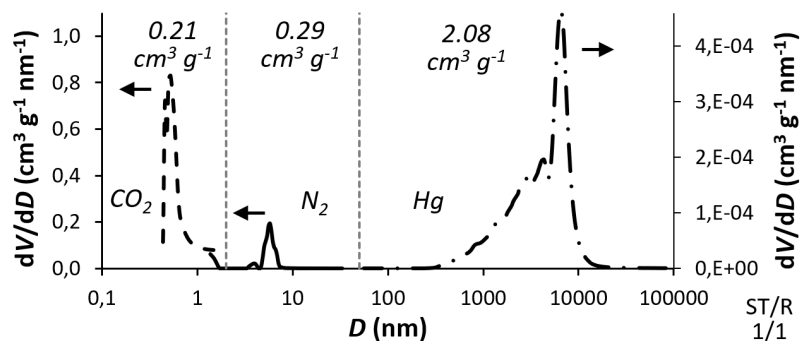


Figure 2 Hierarchical porosity and volumes of micro/meso/macropores of the sample prepared with soft-temple : resorcinol (ST/R) 1/1, dV/dD is pore size distribution, D is pore diameter.

To underline the novelty of the article, the two main contributions can be finally summarised:

- development of an easy synthesis (with omission of using excessive additives or hydrothermal process) of carbon monoliths with hierarchical porosity (microporous or micro- and mesoporous or micro- and meso- and macroporous) by combination of sol-gel and softtemplating processes,
- evidence of the relative importance of mesopores and macropores for (fast) diffusion to the active adsorption sites (micropores/smaller mesopores) in monolithic materials. [1]

Acknowledgements

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References

[1] P. Bulavová, J. Parmentier, V. Slovák, *Microp. Mesop. Mater.* **272** (2018) 155–165.



Integrating Porous Carbon with Ceramics for Sustainable Solutions in Environmental Technologies

S. Perveen*, V. Slovák

University of Ostrava, Faculty of Science, Department of Chemistry, 30. dubna 22, 702 00 Ostrava, Czech Republic

*sajida.ali028@gmail.com

Activated carbons made from biomass are popular for their effectiveness in removing contaminants from the environment, but their use also poses several challenges that need to be addressed. Activated carbon in powdered form is difficult to separate while its pelletized form suffers from significantly reduced adsorption capabilities. One of the potential solutions is to create layers of porous carbon on an appropriate support material. In this research, several methods of synthesis of thin porous carbon layers on ceramic foam as a support were tested. The primary method employed, involved dip-coating of α - Al_2O_3 ceramic foam pieces with appropriate carbon precursors. As a main precursor, commercial wood tar in a mixture with formaldehyde (sample TS) and HCl (THS), oxalic acid (TOS) or both (THOS) was used [1]. For comparison, sucrose (Sc) [2] and phloroglucinol (PGS) [3] solutions were also tested. All the prepared materials were carbonized at 500 °C for one hour in a flow of nitrogen.

Combustion analysis indicated differences in carbon content among the materials, with TS at 2.45%, THS and TOS both at 1.6%, THOS at 1.49%, Sc at 9.85%, and PGS at 4.23%. Although Sc had the highest carbon content, it suffered from a brittle surface layer that easily flaked off. The other samples, however, demonstrated good mechanical stability.

Porosity of prepared materials was characterized by iodine adsorption. When compared to the substrate itself, the samples with carbon layers demonstrated enhanced porosity, following the sequence: PGS > Sc > TS > THS > THOS > TOS.

Application testing was performed by adsorbing methylene blue (MB) from a 50 mL aqueous solution at 15 $\mu\text{mol/L}$, using one piece of the adsorbent, with stirring for 40 minutes. The absolute amount of methylene blue adsorbed per piece of the tested material was converted to grams of carbon present in the surface layer (Figure 1).

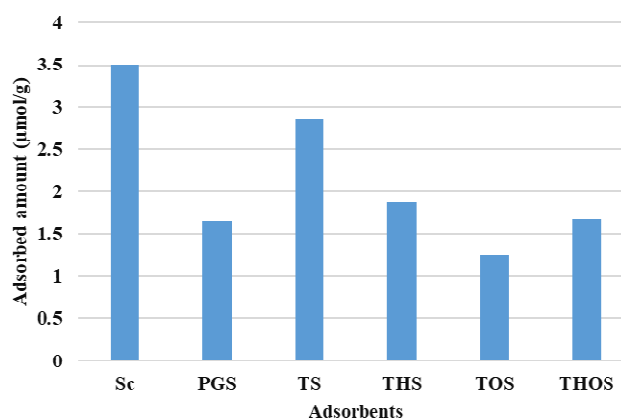


Figure 1 Adsorbed amount of methylene blue on prepared samples (related to g of carbon present in surface layer).

Under the given conditions, the sucrose-based sample was identified as the most effective adsorbent. Considering its mechanical instability, the wood tar-based samples appear to be a more suitable option for practical applications. Surprisingly, the preparation without any catalyst (sample TS) yielded the most efficient adsorbent in this series. This study concludes the applicability of biomass tar for very simple making thin and



porous carbon layers on the ceramic support. Optimizing the synthetic procedure promises obtaining cheap, efficient and easy to handle adsorbent for water remediation.

Acknowledgement

This work was supported by the students' project SGS09/PŘF/2024 (University of Ostrava).

References

- [1] W.M. Qiao, et.al., *Energy & Fuels* **19** (2005) 2576.
- [2] L. Wei, N. Nitta, G. Yushin, *ACS Nano* **7** (2013) 6498.
- [3] S. Kataoka, et.al., *Colloids Surf. A* **347** (2009) 142.



The Influence of the Flow Rate of the Inert Atmosphere During Pyrolysis on the Porosity of Carbonaceous Materials

S. Kowalczyk*, V. Slovák

Department of Chemistry, Faculty of Science, University of Ostrava, 30. Dubna 22, 702 00 Ostrava, Czech Republic

*themimoweicz@gmail.com

The objective of this work was to investigate the influence of the nitrogen flow rate during the pyrolysis of organic substances on the surface properties of the resulting carbon materials. Biomass samples (sawdust, coffee), pure cellulose, and resorcinol-formaldehyde (RF) gel were pyrolyzed using thermal analysis at varying pyrolysis temperatures (500, 800, and 1100 °C) and nitrogen flow rates (0, 10, 100, and 200 cm³/min). Additionally, pyrolysis was conducted in a laboratory tubular furnace at 900 °C with nitrogen flow rates of 20 and 200 cm³/min. The surface properties of the resulting carbons were characterized by iodine adsorption. The samples pyrolyzed in the laboratory furnace were further analyzed using thermoporometry and N₂ adsorption at 77 K. Application tests were conducted for carbon dioxide capture and methylene blue adsorption.

Preliminary iodine adsorption results showed that reducing the nitrogen flow rate significantly enhanced the porous characteristics of the carbon materials, with this improvement becoming more evident at higher pyrolysis temperatures. Nitrogen adsorption measurements further confirmed that biomass-derived carbons produced at a lower flow rate (20 cm³/min compared to 200 cm³/min) can drastically improve microporosity, as illustrated in Fig. 1. The positive effect was further confirmed for the coffee sample in carbon dioxide capture and for the RF gel and sawdust samples in methylene blue adsorption. However, electron microscopy did not reveal any notable changes in the structure or surface morphology of the samples.

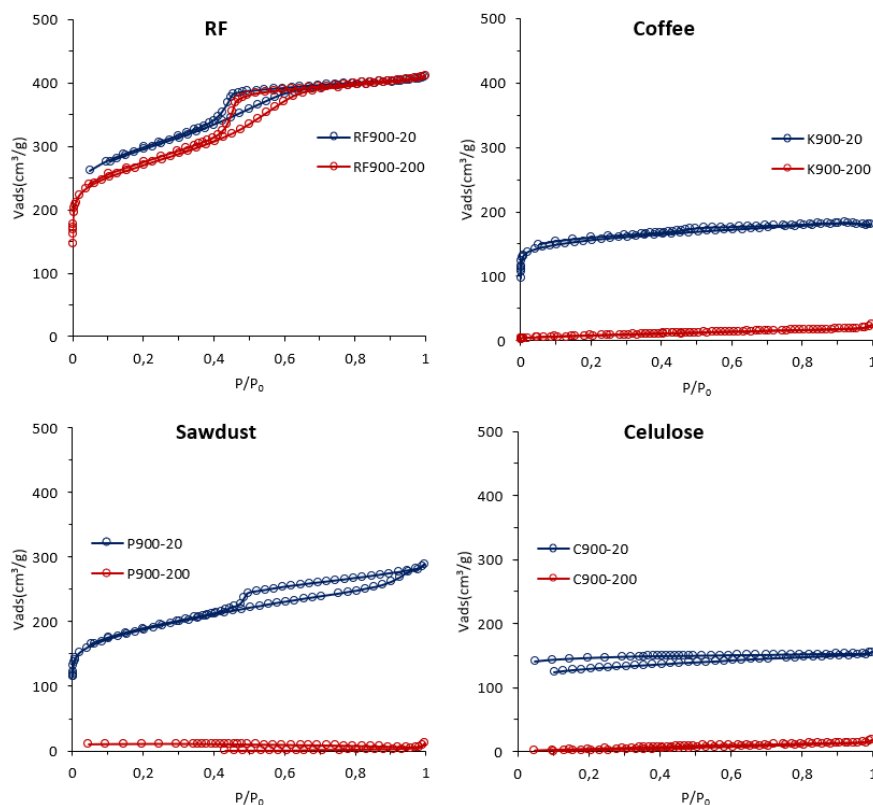


Figure 1 N₂ adsorption isotherms at 77 K. Effect of different nitrogen flow rate during pyrolysis.



In conclusion, lower nitrogen flow rates during pyrolysis not only improve the surface properties of the carbon materials but also offer economic benefits by reducing gas consumption.

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On the Low-Pressure Hysteresis in Gas Sorption Isotherms of Porous Carbons

T. Zelenka^{a*}, L. Zelená^{a,b}, C. Abreu Jaureguí^c, J. Silvestre-Albero^c, G. Zelenková^a, V. Slovák^a

^aDepartment of Chemistry, Faculty of Science, University of Ostrava, 30. Dubna 22, 702 00 Ostrava, Czech Republic

^bDepartment of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

^cLaboratorio de Materiales Avanzados, Departamento de Química Inorgánica-Instituto Universitario de Materiales, Universidad de Alicante, E-03690 San Vicente del Raspeig, Spain

*tomas.zelenka@osu.cz

This study investigates the origin of low-pressure hysteresis (LPH) in the adsorption and desorption of three different probe molecules: CO₂, N₂, and Ar, across various adsorption temperatures (from cryogenic to room temperature), and within five different carbon materials: synthetic carbons (pristine and one post-synthetically oxidized) and natural coal. Significant attention is dedicated to elucidating LPH in oxidized samples outgassed at various temperatures (120–350 °C). Experimental results show that insufficient outgassing temperature can lead to unreliable data due to artificial LPH and significantly underestimated textural properties, primarily caused by porosity blockage from substances like moisture. Conversely, in samples where heteroatoms have a stabilizing effect of texture, such as natural coal, careful consideration of outgassing temperature is crucial due to the risk of thermal degradation. Other factors contributing to LPH are adsorption temperature, and especially, kinetic limitations at cryogenic temperatures for cellulose-based carbons. Minor factors responsible for LPH are the physical state of the sample (monolith vs. powder) and the flexibility of the porous system, both studied by CO₂ sorption.

This study constitutes an important piece in the evaluation of LPH, providing practical recommendations and underlining the importance of experimental design, with implications for further research in this complex field [1].

Acknowledgements

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References

[1] T. Zelenka, L. Zelená, C.A. Jaureguí, J. Silvestre-Albero, G. Zelenková, V. Slovák. *Small*. **20** (2024) 2311990.



Tools for Determination of Wet Materials Porosity

V. Slovák*, G. Zelenková, E. Kinnertová, L. Kořená

Department of Chemistry, Faculty of Science, University of Ostrava, 30. Dubna 22, 702 00 Ostrava, Czech Republic

*vaclav.slovak@osu.cz

This study explores advanced methods for characterizing the porosity of wet materials, with a focus on differential scanning calorimetry (DSC) thermoporometry and ^1H nuclear magnetic resonance (NMR) relaxometry. The research aims to address the challenges of accurately measuring porosity in materials that retain moisture, where traditional methods may fall short.

DSC thermoporometry [1,2] leverages the Gibbs-Thomson equation to determine melting points and crystal sizes, providing insights into pore size distribution through analysis of DSC peak positions, areas, and shapes. The technique's sensitivity to surface chemistry and probe liquid interactions is highlighted, with water, benzene, and octamethylcyclotetrasiloxane discussed as effective probe liquids for various pore sizes and surface chemistries.

NMR relaxometry [3] is presented as a complementary method, utilizing relaxation times (T_2) of nuclei, particularly ^1H in water, to infer the size and distribution of liquid phases within the pores. This technique offers rapid analysis with minimal sample preparation, making it suitable for a range of pore sizes from micro to macro scales.

The study compares the effectiveness, cost, and time efficiency of DSC and NMR methods, highlighting their respective advantages and potential limitations. The findings suggest (Fig. 1) that integrating both techniques can provide a comprehensive understanding of wet material porosity, aiding in the development of more accurate and reliable characterization methods.

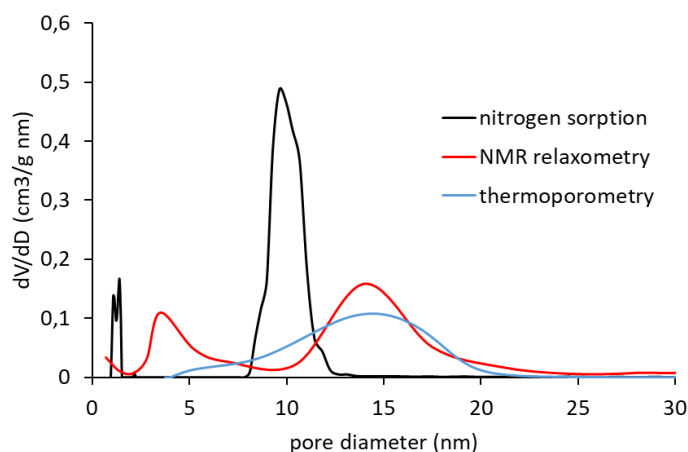


Figure 1 Comparison of various techniques of pore size distribution determination.

Acknowledgements

This work was supported by project LUASK22049 (INTER-EXCELLENCE II, MŠMT).

References

- [1] L. Korena, V. Slovak, G. Zelenkova, *Microp. Mesop. Mater.* **367** (2024) 112977.
- [2] G. Zelenkova, V. Slovak, *Microp. Mesop. Mater.* **366** (2024) 112946.
- [3] E. Kinnertova, V. Slovak, T. Zelenka, et al. *Materials* **15** (2022) 9021.



MIL-101-based Mesoporous Materials for Energy Storage

N. Hlávková*, N. Király, M. Almáši

Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

*nina.hlavkova@student.upjs.sk

Synthesis of metal-organic frameworks (MOFs) is one of the responses modern chemistry gives to the needs of society which are very diverse nowadays. Likewise, there is a demand for solutions to global problems there also is a need to come up with more sustainable and green chemistry and therefore new methods need to be developed to meet the requirements of society. Metal-organic frameworks are a large group of polymeric porous materials which have been intensively studied for the last few decades. The interest in studying these materials lies mostly in a wide range of their applications. MOFs are materials that are composed of metal ions or clusters (known as secondary building units, SBUs) and organic ligands (different organic acids are used very frequently) that can be connected to form one-, two- or three-dimensional lattices. There are many possible options for structures of MOFs and due to their pore volume and surface area, they found their use in various fields of study such as electrochemistry (Li-S batteries), heterogenous catalysis, environmental remediation, as a possible solution for hydrogen storage etc. Finding new methods of efficient hydrogen storage is important these days as hydrogen has become one of the most promising candidates as regards the potential replacement of fossil fuels. Their enormous use for the last few decades has caused not only a rapid decrease in its supply but also because of massive carbon dioxide emission which has very negatively affected climate change. MOFs can adsorb and store hydrogen molecules in their pores with high capacity and safer storage.

In our work, we focused on the preparation of specific types of MOFs known as MILs (Materials Institute Lavoisier). We prepared and characterized seven different types of MIL-101 materials containing Cr(III), Al(III) and Fe(III) ions as SBUs and terephthalic/2-aminoterephthalic acid as organic linkers. The goal of our work was to find one or more materials of this type to be further used as an efficient hydrogen storage material.

All the materials were characterised by IR spectroscopy, PXRD and nitrogen adsorption/desorption measurements (see Fig. 1). As can be seen in Figure 1, the best textural properties were obtained for MIL-101(Cr) materials prepared under basic conditions using tetramethylammonium hydroxide (TMAOH, see red curve in Figure 1, $S_{BET} = 2852 \text{ m}^2/\text{g}$) and neutral conditions (green curve in Figure 1, $S_{BET} = 2593 \text{ m}^2/\text{g}$). Therefore, we consider using these two materials for further research in energy storage problematics focused on hydrogen storage.

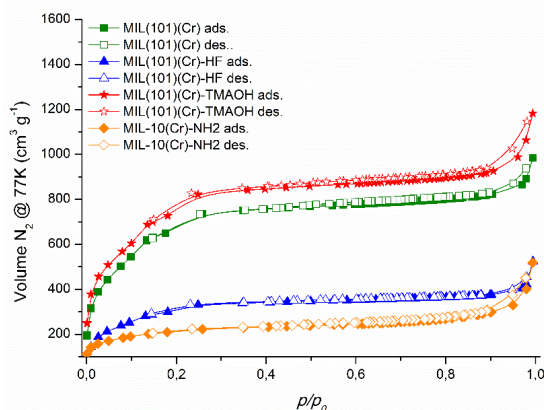


Figure 1 Nitrogen adsorption/desorption isotherms of prepared MIL-101 materials.

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Cellulose-amine Carbon-based Porous Materials for Carbon Dioxide Storage

S. Krupšová^{a*}, M. Almáši^b

^aNovy PORG Gymnasium, Pod Krcským lesem 25, 142 00 Prague, Czech Republic

^bDepartment of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

*krupsovas@gmail.com

The rapidly increasing production of anthropogenic carbon dioxide is a major factor related to global climate change. Capture of carbon dioxide after combustion is a potential solution for reducing CO₂ emissions. However, the currently applied technology is not ecologically or economically sustainable due to the dependence on liquid amines, which brings with them many disadvantages such as an energy-intensive synthesis process and low recyclability. That is why it is necessary to focus on the development of an effective, ecological, and cheap material for capturing CO₂. Recently, activated carbon-based sorbents have gained increased attention due to their unique physicochemical properties such as large specific surface area, tunable pore distribution, and the possibility of simple chemical activation to increase the affinity to CO₂ molecules.

Six activated carbon samples with different textural properties were prepared by hydrothermal and thermal activation using three different amines as *in-situ* N-doped precursors. The synthesis consisted of mixing cellulose and amine (diethylenetriamine, 1,2-bis(3-aminopropylamino)ethane, melamine) in a ratio of 1:1 and their subsequent reaction at 240°C. The resulting materials were hydrothermal products, designated as C+DETA, C+BAPE, C+MELA. The preparation of pyrolyzed products (C+DETA (P), C+BAPE (P), C+MELA (P)), consisted of the same initial synthesis and subsequent chemical KOH activation and pyrolysis in an argon atmosphere at 800°C. The resulting materials were characterized by CHN elemental analysis, IR spectroscopy, TG, SEM and N₂ adsorption measurements. Their CO₂ adsorption capacities were subsequently determined at 0 and 25°C (1 atm). The recyclability of the sample with the highest adsorption capacity was investigated using five cycles of adsorption/desorption measurements with argon flushing and thermal regeneration.

Fig. 1 shows the CO₂ adsorption/desorption isotherms measured at 0°C for hydrothermal (Fig. 1a) and pyrolyzed (Fig. 1b) materials together with the corresponding adsorption capacities of the prepared samples (Fig. 1c) at 1 atm. As can be seen from Figure 1c, hydrothermal products show a higher adsorption capacity, with the highest capacity of 32.3 wt. % was measured on the C+MELA sample. CO₂ adsorption measurements were also determined for hydrothermal products at a temperature of 25°C, with the highest value of 20.43 wt. % was also observed on the C+MELA sample.

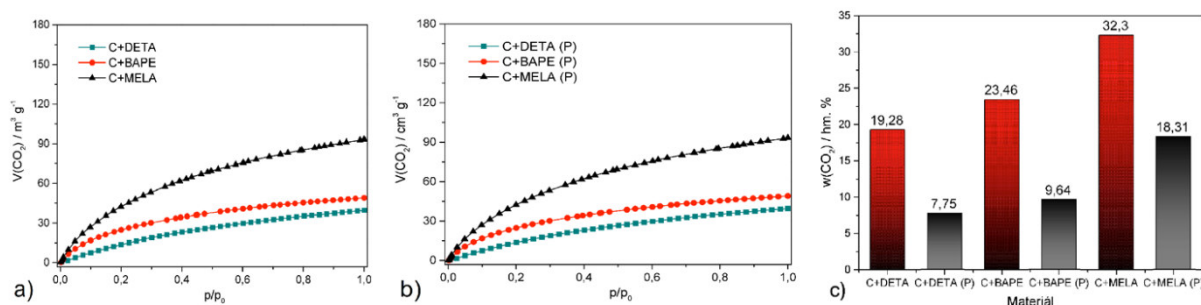


Figure 1 Carbon dioxide adsorption/desorption isotherms at 0 °C for a) hydrothermal and b) pyrolyzed products, c) resulting CO₂ adsorption capacities of hydrothermal and thermal samples at 0 °C and 1 atm.

Regeneration measurements demonstrate the high recyclability of C+MELA, as the sample retains its original adsorption capacity at 25 °C during five CO₂ adsorption/desorption cycles. Thermal regeneration led to the complete regeneration of the product. The argon purge regeneration shows a partial residual residue (7 wt %), indicating incomplete product regeneration, which arose from the formation of covalent bonds between the secondary amines and CO₂ during the adsorption process.



In this work, the effect of activation method on the development of physio-chemical properties and CO₂ adsorption capacity of activated porous carbons was investigated. It was found that while thermal activation led to the significant enhancement of the textural properties of the materials, high activation temperature applied during the pyrolysis resulted in a notable decrease in amines (nitrogen) content, which led to a weakened affinity to CO₂ molecules, resulting in lower adsorption capacity. On the other hand, one-step hydrothermal activation resulted in the development of highly porous products with significantly greater CO₂ adsorption capacities at both 0 and 25 °C. Therefore, it can be concluded that hydrothermal activation represents a promising approach to addressing environmental and economic impacts associated with the synthesis of biomass-based porous materials for CO₂ capture.

The highest CO₂ adsorption capacity 32.3 wt. % was reported on melamine-containing activated carbon (C+MELA) at 0 °C and 1 bar. Apart from effective capturing ability, this sample also displayed a well-developed porous matrix, low production cost, and high recyclability, which, in the case of its application in large-scale CO₂ capture, can significantly reduce the industrial expenses related to material purchase and waste regulation.

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PEI-Schiff Base-modified SBA-12, 15 and 16 Silica for Toxic Metal Capture: Morphology, Modification and Kinetics

L. Zauska^{a*}, M. Almasi^a, P. Pillárová^a, T. Zelenka^b

^aDepartment of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

^bDepartment of Chemistry, Faculty of Science, University of Ostrava, 30. Dubna 22, 702 00 Ostrava, Czech Republic

*lubos.zauska@student.upjs.sk

Mesoporous silica material (MSM) materials are a class of porous structures with uniform and highly organized pore arrangements, typically in the nanometer range. These materials are synthesized using templating methods, where surfactants or polymers guide the formation of the pores. MSM materials, such as SBA-12, SBA-15, and SBA-16, offer high surface areas, tunable pore sizes, and chemical stability, making them ideal for applications in catalysis, adsorption, and drug delivery. Their versatility allows for further functionalization, enhancing their effectiveness in capturing toxic metals or other contaminants [1-2].

A series of SBA materials (SBA-12, SBA-15, and SBA-16) were successfully prepared and modified with polyethyleneimine (PEI) and its Schiff base variants using salicylaldehyde (PS). The materials were characterized using Fourier-transform infrared spectroscopy (FT-IR) and thermogravimetric analysis (TGA) to determine the organic coating. Textural properties, structure, and morphology were studied through nitrogen adsorption/desorption analysis, bright field scanning transmission electron microscopy (BF-STEM) (see fig. 1) and small-angle X-ray scattering (SAXS). X-ray fluorescence analysis (XRF) confirmed the capture of heavy metal ions in the materials' pores, while nitrate anions were identified via FT-IR. Kinetic studies using conductometric analysis (CA) revealed that the adsorption processes followed non-linear decreasing trends, particularly in PS-modified SBA systems and some unmodified samples.

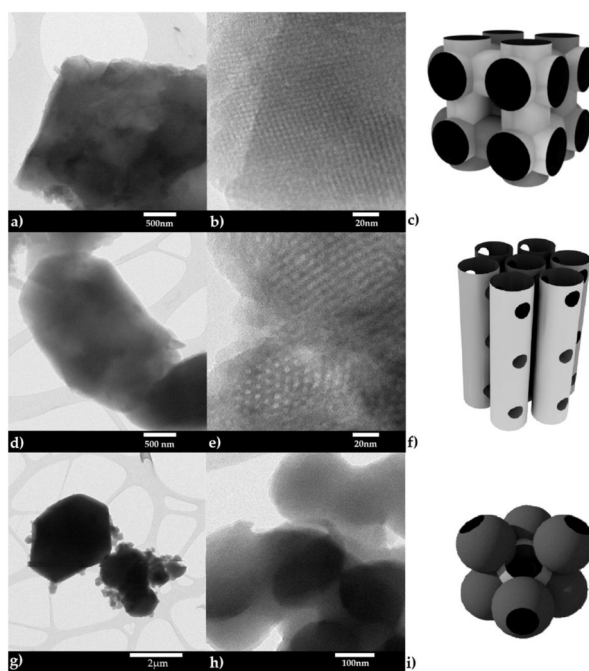


Figure 1 BF-STEM images display the following: (a) SBA-12 particle shape, (b) SBA-12 pores, and (c) a graphical representation of the 3D pore structure of SBA-12. Similarly, (d) SBA-15 particle shape, (e) SBA-15 pores, and (f) a graphical illustration of the 2D pores.



MOFs for Energy Storage

M. Almáši

Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

*miroslav.almasi@upjs.sk

The demand for efficient energy storage solutions has spurred research into novel materials, and metal-organic frameworks (MOFs) have emerged as promising candidates in this domain. MOFs, with their tunable structures and diverse functionalities, present unique opportunities for enhancing energy storage technologies. The unique properties of MOFs, such as high surface area, porosity, pore size/dimensionality, and structural flexibility, make them ideal candidates for addressing the challenges associated with traditional energy storage materials. The presentation will focus on incorporating MOFs into various energy storage and energy reduction systems, including hydrogen storage, lithium-sulfur batteries, magnetic refrigeration and heat pumps. The unique adsorption properties of MOFs enable efficient storage and release of hydrogen, addressing challenges associated with safe and compact storage in the pursuit of advancing hydrogen-based energy systems. The synergistic combination of MOFs as additives in Li-S batteries has shown significant improvements in energy storage performance, including enhanced charge/discharge rates, increased capacity, and prolonged cycle life. The tunable properties of MOFs, including magnetic behaviour, make them promising candidates for use in magnetic refrigeration cycles. By harnessing the unique magnetic characteristics of certain MOFs, it is possible to develop more efficient and environmentally friendly refrigeration technologies with reduced energy consumption and environmental impact. Moreover, MOFs exhibit exceptional water adsorption capacities, and by harnessing the reversible water adsorption-desorption cycle, it is possible to develop energy-efficient heat pump systems for sustainable heating and cooling applications. The insights gained from our investigation contribute to the fundamental understanding of MOF-based energy storage and pave the way for developing next-generation energy storage devices with improved efficiency and sustainability.

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MOFs Constructed from a Tetrahedral-based Linker for Gas Adsorption and Catalysis

M. Almáši*, N. Király, N. Vargová

Department of Inorganic Chemistry, Faculty of Science, P. J. Safarik University, Moyzesova 11, 040 01 Kosice, Slovak Republic

*miroslav.almasi@upjs.sk

Metal-organic frameworks (MOFs) have emerged as an interesting new class of hybrid materials that hold great promise in many applications, including gas storage, catalysis, chemical sensing and drug delivery. MOFs provide an unprecedented level of synthetic tunability, which allows for the incorporation of limitless building blocks to generate novel functional materials.

Usually are MOFs constructed from commercially available linear or bent poly(carboxylic acid)s, which act as linkers between metal ions or their clusters to give final 3D porous structures. However, the demand to better control the final framework architecture leads to the design and synthesis of new linkers with specifically tailored dimensionality. Among them, the ligands with tetrahedral symmetry have received considerable interest recently because they are by nature 3D and extended linkers.

In order to take advantage of the robust network topology, we have constructed MOFs based on bridging bulky ligands of tetrahedral geometry and different transition/nontransition metals [1-3]. The use of the different extended tetrahedral linkers is demonstrated to result in the formation of a 3D microporous networks. Significant structural and topological diversity between the frameworks was observed, and this is shown to be dependent upon the choice of metal centre and the reaction conditions. The textural properties were studied using nitrogen or argon adsorption/desorption measurements and gas adsorption properties of prepared compounds were also investigated by low/high pressure adsorption of carbon dioxide and methane at different temperatures and pressures up to 26 bar. Moreover, selected compounds with coordinatively unsaturated sites were tested as heterogeneous catalysts in Knoevenagel condensation. An interesting size-selectivity screen has been observed revealing the relationship between the size of the substrates and the catalytic activity of the compounds in the Knoevenagel condensation of different bulky aldehydes (n-heptanal, cyclohexane carbaldehyde, benzaldehyde, 4-tert-butylbenzaldehyde, 3,5-ditert-butylbenzaldehyde, 2-naphthaldehyde) with active methylene compounds (malononitrile, methyl cyanoacetate and ethyl acetoacetate) at different temperatures (70–130 °C). Described interesting results of adsorption and catalytic measurements will be presented more in detail.

Acknowledgements

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References

- [1] M. Almáši, V. Zeleňák, A. Zukal, J. Kuchár, J. Čejka, *Dalton Trans.* **45** (2016) 1233-1242.
- [2] M. Almáši, V. Zeleňák, R. Gyepes, S. Bourrelly, M.V. Opanasenko, P.L. Llewellyn, J. Čejka, *Inorg. Chem.* **57** (2018) 1774-1786.
- [3] M. Almáši, V. Zeleňák, M. Opanasenko, J. Čejka, *Catal. Lett.* **148** (2018) 2263-2273.



Enhanced Photocatalytic Degradation of Methylene Blue and Congo Red by Mesoporous Silica-TiO₂ and CoTiO₃: Effects of Dye Concentration, Catalyst Mass and Kinetics

L. Zauska^{a*}, M. Almasi^a, D. Volavka^b, T. Zelenka^c

^aDepartment of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

^bDepartment of Solid State Physics, Faculty of Science, P. J. Šafárik University, Park Angelinum 9, 041 01 Košice, Slovak Republic

^cDepartment of Chemistry, Faculty of Science, University of Ostrava, 30. Dubna 22, 702 00 Ostrava, Czech Republic

*lubos.zauska@student.upjs.sk

Catalysis has a critical role in industries, from chemical manufacturing to environmental applications. Most catalytic reactions are also heavily reliant on the choice of catalyst and support material for its efficiency and selectivity. Among the numerous materials explored as supports of catalysts, mesoporous silica draws much attention due to its different properties. Mesoporous silica can be considered as an ideal platform because of its high surface area, ordered pore structure, and well-tunable porosity. It is supposed to be relatively versatile in a wide variety of catalytic applications, besides thermal or chemical stability, as a host for different kinds of metal nanoparticles, enzymes, and other catalytic species.

The study explored using SBA-15 mesoporous silica as a support for photoactive materials, specifically TiO₂ and TiO₂/CoTiO₃ composites. Photocatalytic composites (SBA-15_1, SBA-15_2, SBA-15_3) with varying amounts of TiO₂ and CoTiO₃ were prepared and characterized. The results confirmed successful fabrication and showed a reduction in texture properties as TiO₂/CoTiO₃ content increased. XPS and EDX analysis identified Ti(III) and Co(II) dopants, which contributed to enhanced photocatalytic activity compared to commercial Aeroxide® P-25 TiO₂ [1-2].

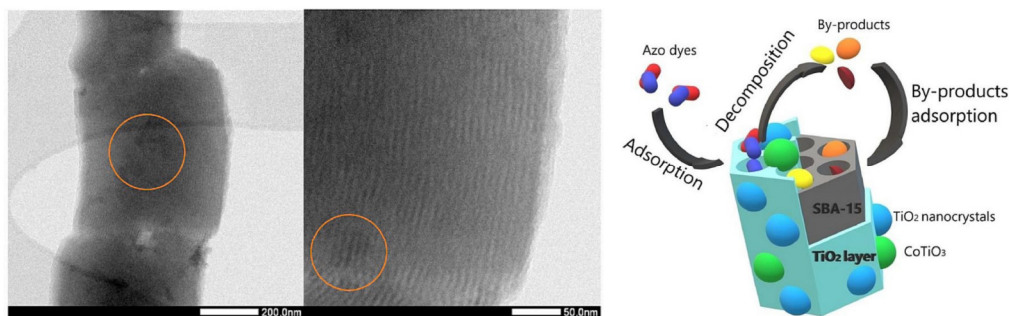


Figure 1 BF-STEM images of SBA-15_1 with different magnifications and graphical representation of SBA-15_1.

The kinetic analysis confirmed that azo dyes like methylene blue and Congo red are effectively and quickly photodegraded. SBA-15_1 showed 30% higher efficiency in degrading methylene blue compared to P-25. It degraded 1.1 mg g⁻¹ at 10 mg L⁻¹ and 27.6 mg g⁻¹ at 50 mg L⁻¹, corresponding to 11% and 55.2% degradation. Congo red showed similar trends with 12.2% and 21.8% degradation. A synergistic effect was observed in the 1:1 dye mixture (MB and CR), removing 27.8 mg g⁻¹ for MB and 25.5 mg g⁻¹ for CR at 254 nm (see Fig. 2). UV radiation at 254 nm achieved better results than 380 nm, and SBA-15_1 maintained catalytic activity after five cycles, enhancing its economic and ecological viability.

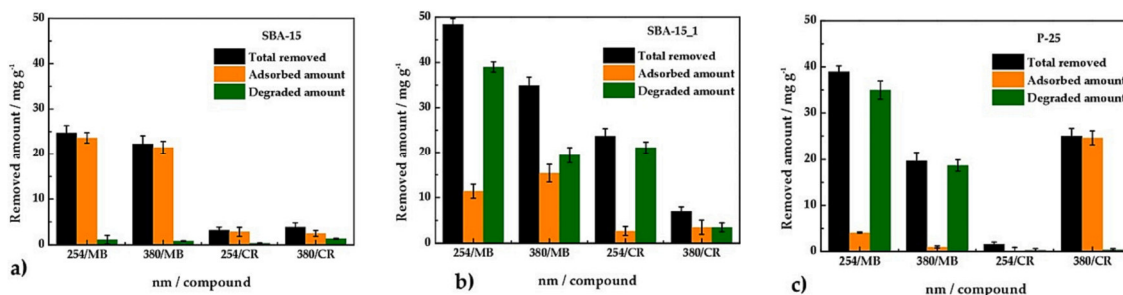


Figure 2 Comparison of photocatalyst effectivity during catalysis under different wavelength radiation (254 and 380 nm) for a) SBA-15, b) SBA-15_1 composite and c) Aeroxide® P-25.

The CoTiO₃/TiO₂-SBA-15 composite enhances adsorption and photocatalytic degradation by improving light absorption and reducing collisions between hydroxyl radicals and pollutants (see Fig. 3). Under visible light, the composite generates hydroxyl radicals, which degrade methylene blue (MB) and congo red (CR) into CO₂ and H₂O. CoTiO₃ plays a key role in increasing visible light absorption and enhancing electron-hole separation when combined with TiO₂. Visible light activates CoTiO₃, creating electron-hole pairs, with electrons transferring to TiO₂'s conduction band, producing superoxide radicals (O₂^{•-}). These radicals, along with hydroxyl radicals (•OH), effectively degrade pollutants. The smooth interface between CoTiO₃ and TiO₂ supports charge carrier migration and reduces electron-hole recombination, ensuring efficient pollutant degradation.

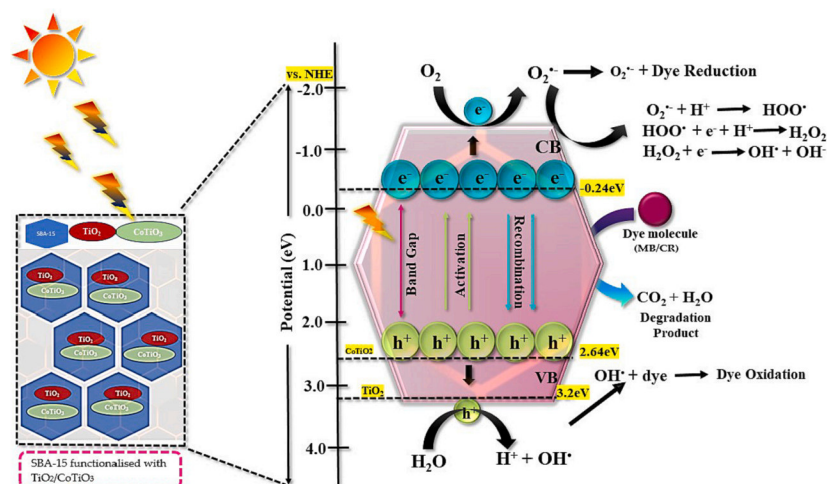


Figure 3 Schematic illustration for charge transfer route, energy band structure, and photocatalytic mechanism of the SBA-15 functionalized with TiO₂ and CoTiO₃

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References

- [1] E. Zauška, D. Volavka, M. Lisnichuk, T. Zelenka, E. Kinnertová, G. Zelenková, J. Bednarčík, V. Zelenák, A. Sharma, S. Nehra, A. Eštoková, M. Almáši, J. Photochem. Photobiol. A **451** (2024) 11522.
- [2] E. Zauška, E. Beňová, M. Urbanová, J. Brus, V. Zelenák, V. Hornebecq, M. Almáši, J. Funct. Biomater. **13** (2022) 275.



Mesoporous Silica Nanoparticles for Adsorption of Drug Residues in Wastewater

E. Beňová^{a*}, V. Zelenák^a, M. Almáši^a, V. Hornebecq^b

^a Department of Inorganic Chemistry, Faculty of Science, P.J. Šafárik University in Košice, Moyzesova 11, 041 01 Košice, Slovak Republic

^b Aix Marseille Univ, CNRS, Madirel, Marseille, France

*eva.benova@upjs.sk

The persistence of pharmaceutical residues in wastewater is a growing environmental concern due to their harmful effects on aquatic ecosystems and potential health risks to humans. Mesoporous silica materials (MSMs) have shown significant promise in the adsorption and removal of drug residues from wastewater, offering a sustainable and efficient solution for water treatment. The large surface area, uniform pore size, and tunable chemical properties of MSMs make them highly effective for capturing a broad range of pharmaceutical compounds, including antibiotics, hormones, analgesics, and psychiatric drugs [1], [2].

Functionalization of mesoporous silica enhances its adsorption efficiency for specific pharmaceuticals. For instance, MSMs functionalized with organic groups like amines, thiols, or phosphonates demonstrate a high affinity for various drug molecules. Amino-functionalized MSMs have been reported to effectively adsorb non-steroidal anti-inflammatory drugs (NSAIDs) such as ibuprofen and diclofenac [3], while thiol-modified silica has been used to capture antibiotics like ciprofloxacin and tetracycline [4]. These materials can be fine-tuned to target drugs with diverse chemical structures, from hydrophilic compounds to hydrophobic pollutants.

In addition to adsorption, MSMs can be engineered to incorporate catalytic functionalities, allowing them to degrade drug residues through photocatalysis or other advanced oxidation processes. For example, metal-doped MSNs, such as those containing TiO₂ or Fe₂O₃, can photocatalytically decompose pharmaceutical compounds in wastewater under UV or visible light, breaking them down into less harmful byproducts [5], [6].

In the presented study, we have prepared several mesoporous silica materials (MSMs) and we studied their potential to adsorb commonly used drugs. We have synthesized highly ordered mesoporous silica materials with hexagonal structure MCM-41 and SBA-15, and SBA-12 with cubic structure. These materials were further modified by organic ligands 7-[(3-triethoxysilyl)propoxy]coumarin (MCM-41_C and SBA-12_C) and N-(propyl)aniline (SBA-15_N-ANI). The structure of the material, as well as surface modifications, influence the adsorption of the drugs. As model drugs, we used non-steroidal anti-inflammatory drug naproxen and antineoplastic agent 5-fluorouracil. The amounts of the adsorbed drugs are presented in the Table 1.

Table 2 The adsorbed amounts of the drugs.

MSMs	DRUG	m _{ADSORBED} (mg/g)
MCM-41_C	Naproxen	399
SBA-12_C	Naproxen	56
SBA-15_N-ANI	Naproxen	36
SBA-15_N-ANI	5-Fluorouracil	42
SBA-15_N-ANI	Naproxen (mixture)	20
SBA-15_N-ANI	5-Fluorouracil (mixture)	62

More over we studied adsorption profiles of the drugs onto prepared materials and we also tested the adsorption of these drugs in their mixture, as various organic molecules are present in wastewater. Examples of adsorption isotherms of studied drugs onto mesoporous silica SBA-15 and SBA-15 modified with N-(propyl)aniline are shown in Figure 1.

As it is clearly shown, there are no differences in adsorption properties for 5-Fluorouracil alone or in mixture; both isotherms, for single 5-Fluorouracil and in a mixture are very similar. For naproxen, the amount of drug adsorbed when it is mixed with 5-Fluorouracil is almost three times larger than when it is adsorbed alone. The samples SBA-15 modified by N-(propyl)aniline has a negative surface charge of -82 mV at pH 7.4. 5-fluorouracil has NH groups which are not deprotonated at pH 7.4 (pKa (5-FU) = 8.02). On the contrary,



naproxen (the pKa (NAP) = 4.15) has a polar carboxylate group so we assume that the adsorption of both drugs is governed by electrostatic interactions and hydrogen bonding with negatively charged particles.

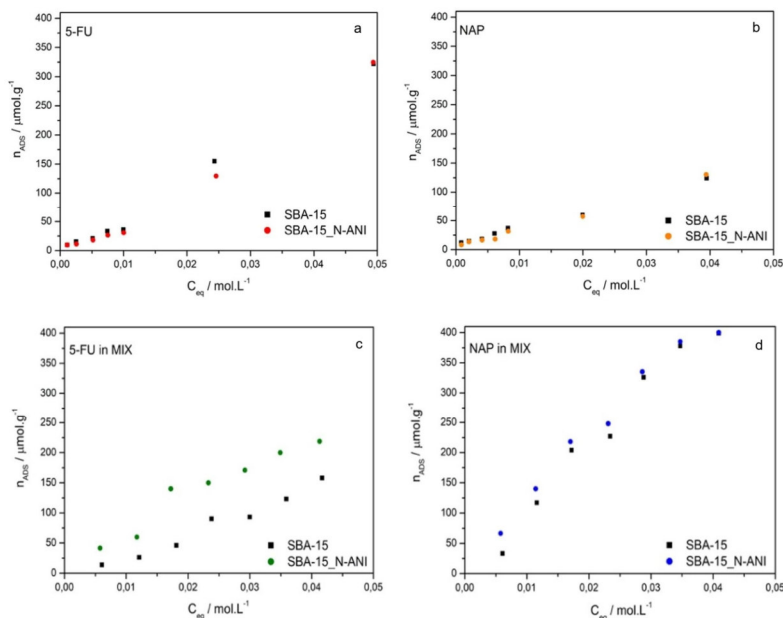


Figure 2 Adsorption isotherms of 5-fluorouracil a), naproxen b), co-adsorbed drugs 5-fluorouracil c) and naproxen d) on SBA-15 and SBA-15 modified by N-(propyl)aniline.

In conclusion, the study demonstrates the effective adsorption of pharmaceuticals, such as naproxen and 5-fluorouracil, onto mesoporous silica materials modified with organic ligands. The results highlight the significant potential of these materials for removing pharmaceutical contaminants from wastewater. With their high surface area, tunable pore structure, and surface modification capabilities, these materials offer an efficient and sustainable approach for addressing pharmaceutical pollution in water. The promising adsorption isotherms further emphasize their suitability for practical applications in environmental remediation.

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References

- [1] A. Grela, J. Kuc, T. Bajda, *Materials* **14** (2021) 17.
- [2] F. Masoudi, M. Kamranifar, F. Safari, A. Naghizadeh, *Desalin. Water Treat.* **169** (2019) 333–341.
- [3] S. Chandrashekar Kollarahithlu, R.M. Balakrishnan, *J. Clean. Prod.* **294** (2021) 126155.
- [4] D. Lu et al., *J. Clean. Prod.* **264** (2020) 121644.
- [5] H. Kumari et al., *Water. Air. Soil Pollut.* **234** (2023) 349.
- [6] B.G. Park, *Gels* **8** (2021) 14.



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