ENMIX WORKSHOP

European Nanoporous Materials Institute of Excellence

Advanced nanoporous materials for industrial leadership

BOOK OF ABSTRACTS

September 12-13, 2024 | Porto, Portugal

Faculty of Engineering - University of Porto

ENMIX

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TITLE
9th European Nanoporous Materials Institute of Excellence Workshop

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PREFACE

The 9th European Nanoporous Materials Institute of Excellence (ENMIX) Workshop will be held from September 12 to 13, 2024, at the Faculty of Engineering of the University of Porto, Portugal. This event is organized by the European Nanoporous Materials Institute of Excellence (ENMIX), with support from the Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials (LSRE-LCM), Associate Laboratory ALiCE, and the Portuguese Chemical Society (SPQ).

ENMIX, established in 2009, is a scientific network dedicated to the advancement of nanoporous materials, uniting expertise in areas such as material synthesis, characterization, and applications. A key focus of ENMIX is fostering the development of PhD students and postdoctoral researchers by facilitating the exchange of knowledge, methods, and materials. To this end, ENMIX Workshops and ENMIX Young Scientist Meetings play a vital role in achieving our mission.

This year's workshop, under the theme “Advanced Nanoporous Materials for Industrial Leadership,” aims to highlight the latest scientific achievements from the participating research groups and strengthen collaborations among ENMIX partners.

The 9th ENMIX Workshop will feature three plenary sessions with world-renowned researchers: João Rocha from CICECO/University of Aveiro, Eleni Iliopoulou from CPERI/CERTH, Thessaloniki, and Atsushi Urakawa from TU Delft. In addition, there will be two invited talks by Alexandre Ferreira from the University of Porto and Petar Djinovic from the National Institute of Chemistry, Ljubljana. The programme also includes a variety of oral and poster presentations, ensuring a highly prestigious scientific event.

We are pleased to announce that during this edition, Eleni Iliopoulou will take on the role of ENMIX CEO, succeeding Elias Klemm from the University of Stuttgart, who has led the network with great enthusiasm for 12 years.

The ENMIX Award 2024, recognizing “the best scientific publication on nanoporous materials, especially their synthesis or use as sorbents, membranes, and/or catalysts” will be awarded to Edgar Stiven Duran-Uribe from the University of Alicante. His winning publication is E.S. Duran-Uribe, A. Sepúlveda-Escribano, E.V. Ramos-Fernández, Microwave-assisted synthesis of CoxP@C catalysts: Application to the hydrogenation of 1-chloro-4-nitrobezene, Chemical Engineering Journal (474) 2023, 145897.

Additionally, the 11th ENMIX Young Scientist Meeting, organized by Charlotte Simms (University of Antwerp), José Luis del Río Rodríguez (Instituto de Tecnología Química, Universitat Politècnica de València) and Aljaž Škrjanc (National Institute of Chemistry, Slovenia), will take place on September 11, 2024, at the Faculty of Engineering of the University of Porto. The programme for this meeting is also included.

The Organizing Committee would like to extend its heartfelt thanks to all participants, with the hope that this meeting will foster new and strengthen existing scientific collaborations among ENMIX partners.

Fernando Pereira (local organizer)
Elias Klemm (old CEO)
Eleni Iliopoulou (new CEO)

Porto, September 12, 2024

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PROGRAMME

FACULDADE DE ENGENHARIA DA UNIVERSIDADE DO PORTO – ROOM B032

	Thursday, 12th September 2024	Friday, 13th September 2024
08:30	Registration	
09:00	Opening Session	
09:15 09:30 09:45	**PL 1** **João Rocha**	**PL 3** **Eleni Iliopoulou**
10:00 10:15	**IL 1** **Alexandre Ferreira**	**IL 2** **Petar Djinovic**
10:30	OC 1 ::: Susan Sen	OC 11 ::: Elias Klemm
10:50 11:00	**Coffee Break**	**Coffee Break**
11:20	OC 2 ::: Aljaž Škrjanc	OC 12 ::: Coset Abreu Jauregui
11:40	OC 3 ::: Cristina Martínez	OC 13 ::: Samar Al Jitan
12:00	OC 4 ::: Pascal Dietzel	OC 14 ::: Nataša Novak Tušar
12:20	OC 5 ::: Monica Jimenez-Ruiz	OC 15 ::: Sofia Santos
12:40	OC 6 ::: Matthias Thommes	**Closing Session**
13:00	**Lunch**	**Lunch**
14:30 14:45 15:00	**PL 2** **Atsushi Urakawa**	
15:15	OC 7 ::: Stefano Cimino	
15:35	OC 8 ::: Luciana Lisi	
15:55	OC 9 ::: Edgar Stiven Duran Uribe	
16:15	OC 10 ::: José Luis del Río-Rodríguez	
16:35 16:55 17:15 17:35	**Poster Session** **& Coffee Break**	
20:30	**Dinner**	

PL: Plenary Lecture (45') • IL: Invite Lecture (30') • OC: Oral Communication (20') (including discussion)

08:30 – 09:00	**Registration**
09:00 – 09:15	**Opening Session**
SESSION 1: Synthesis, Characterization and Separation Processes	
09:15 – 10:00	Plenary Lecture 1 **João Rocha.** University of Aveiro, Portugal. *Zeolites and MOFs: Pore-Fectly Saving the World, One Pore at a Time*
10:00 – 10:30	Invited Lecture 1 **Alexandre Ferreira**. University of Porto, Portugal. *Cyclic Adsorption Processes: Bridging Fundamentals and Applications*
10:30 – 10:50	Oral Communication 1 **Susan Sen.** University of Bergen, Norway. *Porous and Robust Metal-Organoborane Framework*
10:50 – 11:20	**Coffee Break**
11:20 – 11:40	Oral Communication 2 **Aljaž Škrjanc.** National Institute of Chemistry, Ljubljana, Slovenia. *Why nickel dislikes ZIF-8: routes towards preparation of pure nickel zeolitic imidazolate frameworks*
11:40 – 12:00	Oral Communication 3 **Cristina Martínez.** Instituto de Tecnología Química, UPV-CSIC, Valencia, Spain. *The influence of additives derived from zeolite/LDH composites on catalytic cracking of heavy petroleum oils for light olefin production*
12:00 – 12:20	Oral Communication 4 **Pascal D. C. Dietzel.** University of Bergen, Norway. *Direct observation of the dehydration of a metal hydroxido cluster to a metal oxido cluster in a metal-organic framework*
12:20 – 12:40	Oral Communication 5 **Monica Jimenez-Ruiz.** Institut Laue-Langevin, Grenoble, France. *Understanding the Microscopic Mechanism for the Industrially Relevant Ethylene/Ethane Separation by Silver-Containing Molecular Sieves*
12:40 – 13:00	Oral Communication 6 **Matthias Thommes**. Institute of Separation Science & Technology, Friedrich-Alexander - University Erlangen-Nürnberg, Erlangen, Germany. *Assessment of Hydrophilicty/Hydrophobicity in Nanoporous Materials*
13:00 – 14:30	**Lunch**

SESSION 2: Catalysis and Catalytic Processes	
14:30 – 15:15	Plenary Lecture 2 **Atsushi Urakawa**. TU Delft, The Netherlands. *Playing with thermodynamics and kinetics in CO_2 conversion catalysis*
15:15 – 15:35	Oral Communication 7 **Stefano Cimino.** STEMS-CNR, Naples, Italy. *Sulfur Tolerance of Li-Ru/Al_2O_3 Dual Function Material for the Integrated CO_2 Capture and Methanation*
15:35 – 15:55	Oral Communication 8 **Luciana Lisi.** Consiglio Nazionale delle Ricerche, Naples, Italy. *Effect of Pt load and Na addition to ZSM-5 for H_2 SCR of NOx*
15:55 – 16:15	Oral Communication 9 **Edgar Stiven Duran Uribe** Universidad de Alicante, Spain. *Nitroarene Hydrogenation Using Nitrogen and Phosphorus Co-doped Activated Carbon*
16:15 – 16:35	Oral Communication 10 **José Luis del Río-Rodríguez.** Instituto de Tecnología Química, Universitat Politècnica de València, Spain. *Influence of Heteroatom Doping on Heterogeneous Cobalt Catalysts for the One-Pot Synthesis of Benzimidazoles by Reductive Coupling of Dinitroarenes with Aldehydes in Water*
16:35 – 17:35	**Poster Session & Coffee Break**
20:30	**Dinner ::: O Comercial Restaurant - Palácio da Bolsa**

SESSION 3: Electrocatalysis & Photocatalysis	
09:15 – 10:00	Plenary Lecture 3 **Eleni Iliopoulou.** CPERI/CERTH, Thessaloniki, Greece. *Methane pyrolysis: Unlocking the potential for COx-free Hydrogen Production*
10:00 – 10:30	Invited Lecture 2 **Petar Djinovic.** National Institute of Chemistry, Ljubljana, Slovenia. *Visible light assisted CO_2 valorization to CO over metal@oxide semiconductor photocatalysts*
10:30 – 10:50	Oral Communication 11 **Elias Klemm.** University of Stuttgart, Germany. *Electrocatalysis Under Confinement: CO_2-Reduction with Molecular Catalysts Immobilized on Ordered Mesoporous Carbons*
10:50 – 11:20	**Coffee Break**
11:20 – 11:40	Oral Communication 12 **Coset Abreu Jauregui.** University of Alicante, Spain. *Surface Chemistry and Photodegradation: Insights into Heteroatom-Mediated Catalysis*
11:40 – 12:00	Oral Communication 13 **Samar Al Jitan.** University of Antwerp, Belgium. *Photocatalytic conversion of CO_2 to methanol using copper oxide and vanadium oxide co-deposited on titania nanotubes*
12:00 – 12:20	Oral Communication 14 **Nataša Novak Tušar**. National Institute of Chemistry, Ljubljana, Slovenia. *Nanoporous Materials for Fenton-like and Photo-Fenton-like Water Cleaning via Heterogeneous Catalysis*
12:20 – 12:40	Oral Communication 15 **Sofia G. G. Santos.** University of Porto, Portugal. *Green Fabrication of Carbon-Coated Macrostructured Catalysts with Sodium Alginate Assistance*
12:40 – 13:00	Closing Session
13:00 – 14:30	**Lunch**

POSTER SESSION | THURSDAY, 12th SEPTEMBER 2024 | 16h35 – 17h35

P1	Empowering the gas desulfurization efficiency of carbon materials through incorporating active inorganic phases	Meriem Abid
P2	Gas-phase simulated moving bed for methane and nitrogen separation using maxsorb extrudates	Rafael Osório Marques Dias
P3	Grignard Surface Modification: Insights Into The Modification Mechanism And Surface Properties	Femi Rose Tharakan
P4	Analysis of the flowrate effect on the continuous adsorption of diclofenac using carbon nanotubes functionalized with Fe nanoparticles	Heloisa Pereira de Sá Costa
P5	Synthesis of graphene oxide and clay-based nanocomposite for adsorption of emerging pharmaceutical contaminants in water	Nickolly Bukkyo Vieira Serafim
P6	3D-printed Hybrid Monolith for CO_2 Capture	Ana Jorge Meireles Pereira
P7	Mechanochemistry and ZIFs; facile functionalisation of porous frameworks for CO_2 capture	Aljaž Škrjanc
P8	Novel microporous zinc-based MOF for selective CO_2 capture	Klara Klemenčič
P9	Hydrogenation of CO_2 to hydrocarbons with multimetallic carbon catalysts	Mariana Felgueiras
P10	Innovative carbon:Al_2O_3 composite support for catalysts to CO_2 Hydrogenation to Methanol	Ana Rita Nunes Querido
P11	Use of Oxidised Activated Carbon as Metal-Free Catalyst to Obtain Substituted Anilines	Edgar Stiven Duran Uribe
P12	Palladium and Platinum hydrides as catalysts for enyne cyclosiomerization reaction and advanced solid state nmr spectroscopy	Erik Jasper Wimmer
P13	Catalytic Hydrogenation for PFAS Removal	Catarina da Cunha Lopes
P14	Development of 3D printed carbon-based macrostructures through direct ink writing	José Ricardo Monteiro Barbosa
P15	Self-Supporting Films and Powders of Ordered Mesoporous Carbon based on Tailored Polyether Templates for Application in Electrocatalysis under Confinement	Patricia Sonnenberg
P16	Toward High-rate Carbon-based Supercapacitors: New Insights into Tuning Multimodal Mesoporosity in Hierarchical Porous Carbons	Mohammed Saleem Subrati Yadulla
P17	Degradation of pollutants in industrial effluents using ozonation reaction over Fe-catalysts	Ouissal Assila
P18	Proton-Electron Transfer From Well-Defined Molecular Hydrogen Donors To Metal Oxides	Osman Bunjaku

ABSTRACTS

Zeolites and MOFs: Pore-Fectly Saving the World, One Pore at a Time

João Rocha

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Zeolites are porous, crystalline hydrated aluminosilicates with frameworks composed of tetrahedral units connected by oxygen atoms, featuring exchangeable cations. Think of them as the Swiss Army knife of materials science — they are very versatile and widely used in catalysis, gas separation, and ion-exchange. Beyond traditional zeolites, certain microporous silicates are assembled from transition-metal and lanthanide-bearing heteropolyhedra. These materials not only exhibit the conventional properties of zeolites but also demonstrate magnetism and light emission.

This talk will present applications of such materials developed in my laboratory, including light emission devices [1], treatment of hyperkalemia (excess K^+ in serum) with a new drug now on the market [2], slow release of NO for medical applications [3], removal of rare-earth elements from aqueous solutions [4], and membranes for H_2/N_2 gas separation [5].

Enter Metal Organic Frameworks (MOFs). These are hybrid materials with polyatomic metal clusters linked by covalent bonds to form nanoporous structures. Unlike zeolitic materials, MOFs operate under milder conditions and are less robust, but they are more amenable to rational synthesis and post-synthetic modification using conventional organic synthesis methods.

In this talk, I will present some examples of my groups' research on MOFs, including temperature sensing via light emission [6], and uranyl ion capture from waters [7]. Additionally, I will highlight our recent efforts to design efficient electrically conductive MOFs based on the partially oxidised perylene ligands for applications in (opto)electronics, electrocatalysis and energy storage [8], as well as luminescent MOFs based on persistent neutral organic (e.g., triphenylmethyl) radicals that also exhibit magnetic and electrochemical properties [9].

Acknowledgements

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020, and LA/P/0006/2020, financed by national funds through the FCT/MEC (PIDDAC). The NMR spectrometers are part of the National NMR Network (PTNMR) and are partially supported by Infrastructure Project No. 022161.

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Cyclic Adsorption Processes: Bridging Fundamentals and Applications

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The Cyclic Adsorption/Reaction Processes research group at LSRE-LCM has its roots in the ground-breaking work that can be traced back to the origins of LSRE in the 1970s. Renowned globally, we are a leader in the field, forging impactful collaborations with industrial partners such as TOTAL, ExxonMobil, and Samsung. Our research is marked by innovation, addressing crucial industrial challenges across various applications. In this presentation, it will be given focus on the Cyclic Adsorption Processes branch of the group. Separation processes are indispensable pillars in the chemical industry, playing a pivotal role in facilitating the production of top-tier products, mitigating environmental impact, and optimizing resource utilization. These processes are integral across the entire spectrum of chemical manufacturing, from the extraction of raw materials to the distribution of finished products. Cyclic Adsorption Processes represent a cluster of separation technologies extensively applied in various industries, notably Pressure Swing Adsorption and Simulated Moving Bed. Rooted in a sequence of steps involving adsorption onto an adsorbent surface and subsequent regeneration, these technologies form the backbone of efficient separation methodologies. The careful selection and development of tailored adsorbents emerge as crucial milestones in the evolution of new processes or the enhancement of existing ones. Their significance resonates in propelling innovation and meeting the dynamic demands of diverse sectors, including petrochemicals, pharmaceuticals, environmental remediation, and food processing. Introducing novel adsorbents promises elevated selectivity and efficiency in isolating target components from intricate mixtures. This, in turn, contributes to the overall enhancement of separation processes by augmenting adsorption capacity, selectivity, and kinetics. Recent accomplishments in our group include the creation of tailored carbon-based adsorbents for VOCs capture and hexane isomers separation. Furthermore, we've pioneered hybrid structured adsorbents that are applicable to ESA. Collaborations extend into the materials science domain, where partnerships with groups like KRICT and CWK contribute to the rigorous testing of materials. Otherwise, we collaborate with groups strong in the materials science area and test their materials, such as the groups at the KRICT and CWK, an industrial partner. Another critical aspect of our research involves designing novel, more efficient processes and developing personalized mathematical models for process simulation, optimization, and control. By focusing on resource conservation, our endeavors enable the reuse and recycling of valuable materials, reduce raw material consumption and energy use, and foster sustainability in chemical production. Our research spans a diverse array of separation processes, encompassing cryogenic (V)PSA processes for natural gas upgrade or H2 purification from methane streams, carbon dioxide capture, light olefins separation by PSA, and gas-phase SMB in collaboration with ExxonMobil and KRICT. Noteworthy other projects include nitrogen/methane separation for methane upgrade, hexane isomers separation, monomers recovery (including VCM in collaboration with CIRES), water harvesting, separation of chiral compounds, and proteins separation by liquid-phase SMB, the latter in partnership with FLUIDINOVA.

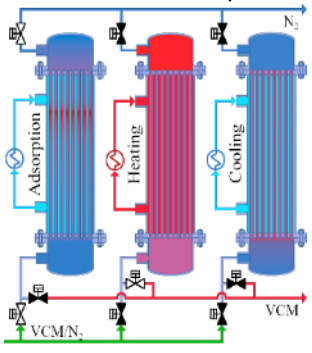

Fig 1. Illustration of a 3-unit MTA system.

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Porous and Robust Metal-Organoborane Framework

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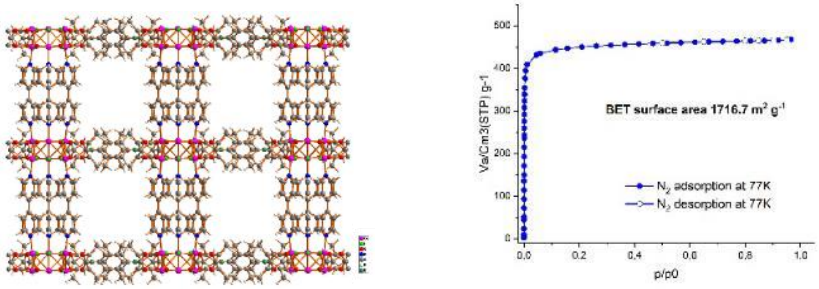
Functionalized porous metal-organic frameworks (FPMOFs) have attracted much attention as an emerging class of microporous materials, exhibiting controlled properties for wide range of applications such as selective adsorption and separation of small molecules, chemical adsorption, electronics, drug delivery and catalysis [1], [2]. The utilities of FPMOF are mostly attributed to their large internal functionalized surface areas and permanent porosities. The constructions of stable functionalized porous MOFs with tailored properties for specific applications are still a fundamental challenge. To address it, a number of strategies have been developed to design and synthesize FPMOFs [3]. One of these is the construction of pillar-layered MOFs [4]. It appears to be especially promising for the synthesis of stable and porous FPMOFs with tunable pore size.

In this work, we adopted the pillar-layered strategy to develop functionalised FPMOFs by reasonable selection of organic linkers and the secondary building unit. The Lewis acidic C_3-symmetric tritopic 4,4',4''-boranetriyltris(3,5-dimethylbenzoic acid) (BTTDMBA) and Co(II) based Co_6F_6-cluster form the layers, while 4,4'-bipyridine (BPY) is used as pillaring linker to connect them, resulting in a Lewis acid functionalized porous MOF, Co-BTTDMBA-BPY. The stable Co_6F_6-cluster, each of which is pillared by three BPY in each direction, and tritopic carboxylate linker increase the stability of the rigid framework. The BTTDMBA linker functionalizes the internal surface with a Lewis acidic site. Low temperature N_2 adsorption study reveals a high specific surface area (BET surface area = 1717 m^2 g^{-1}) with total pore volume of 0.676 cm^3 g^{-1}. The performance in carbon capture, and ethane and ethylene sorption were also evaluated and variable temperature in-situ X-ray diffraction performed.



(a) (b)

Fig.1.a) Co-BTTDMBA-BPy MOF; **b)** N_2 adsorption isotherm at 77K

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Why nickel dislikes ZIF-8: routes towards preparation of pure nickel zeolitic imidazolate frameworks

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Herein we report the successful syntheses of the first pure nickel ZIFs with zeolitic RHO (NICS-21) and SOD (NICS-22) topologies. The hypothesis that linkers with additional functional groups that have the ability to coordinate to Ni2+ would complete nickel coordination octahedra and stabilise the framework was tested and confirmed. With future work on extending carboxyl-functionalised linkers to other coordinating functional groups that would allow the metal to stabilise in its preferred coordination state, we could possibly further expand the range of potential ZIF forming metal nodes. Both materials under investigation exhibit high thermal stability and permanent porosity, with comparable SBET and CO_2 uptakes to their closest Zn analogues. The prepared materials were then successfully used as heterogenous catalysts in Suzuki-Miyaura coupling reactions, showing promising activity for both materials and, in the case of NICS-21, reusability as well. Moreover, an important advantage of the developed Ni-based ZIFs lies in the ease of their synthesis and the conditions that they require to be catalytically active, i.e. our catalysts allow for the preparation of potentially high-value precursors and intermediates with high yields under mild conditions in selected types of Ni-catalysed transformations. Furthermore, NICS-22`s high $CO_2$ uptake and NICS-21`s high water uptake could potentially allow for additional investigation into sorption applications.

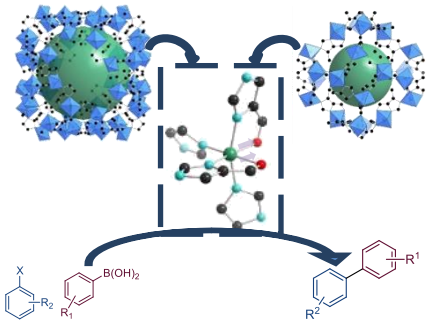

Fig. 1. Representation of NICS-21 structure containing LTA cage (left) and NICS-22 structure containing SOD cage (right) with pore sizes of 9.5 Å and 5.8 Å respectively, indicated by green balls. The six-fold coordination environment of nickel(II). Representative Suzuki-Miyaura cross-coupling reaction(bottom).

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The influence of additives derived from zeolite/LDH composites on catalytic cracking of heavy petroleum oils for light olefin production

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Light olefins, especially propylene, are key building blocks in the petrochemical industry [1], mainly produced via steam cracking of hydrocarbons [2] or fluid catalytic cracking (FCC) of heavy feedstocks such as vacuum gas oil (VGO) [3]. The latter process presents the advantages of its ability to handle heavy oil fractions and to selectively adjust the product distributions [3c]. One of the most cost effective and efficient routes to enhance light olefins yield is the addition of catalyst additives to USY-based FCC catalysts. The medium pore zeolite ZSM-5 is one of the most studied FCC additives, producing predominantly propene and butenes [3b] but also light alkanes by undesired bimolecular hydrogen transfer reactions. Thus, the design of new additives with higher selectivity to LPG olefins is of high interest.

Herein, we have designed an efficient additive based on a composite material derived from ZSM5 and layered double hydroxides (Z5-LDH). The increase in LPG olefin production is attributed to the lower Brønsted acid sites and acid strength in Z5-LDH, which minimizes secondary reactions such as hydrogen transfer. Moreover, the basic metal oxide generated from the LDH material suppresses the re-adsorption of produced LPG olefins, reducing their conversion and increasing their final yield. This additive has shown benefits not only in VGO cracking but also in the conversion of other heavier feedstock such as ATM residue.

Acknowledgements

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Direct observation of the dehydration of a metal hydroxido cluster to a metal oxido cluster in a metal-organic framework

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Some metal-organic frameworks (MOFs) exhibit single-crystal-to-single-crystal transformations during removal or exchange of the guest molecules in the pores. Crystal structure determination of such samples is a powerful technique to elucidate the host-guest properties of the MOF. Typically, adsorption sites or configurational changes in network arrangement can be identified. Cases where the constitution of the network changes are much rarer.

Here, we present the desolvation and dehydration of a zinc-organic framework $[Zn_4(OH)_2(solv)_2]L{\cdot}solv$ (L = organic linker, solv = solvent molecules), in which the constitution and geometrical arrangement of the inorganic secondary building unit (SBU) is completely changed upon heating of the material. In as-synthesized state, the inorganic SBU has coordinated solvent molecules on zinc cations. Originally, we expected that solvent removal at elevated temperature would result in these coordination sites becoming available as open metal sites for host-guest interactions. However, a single crystal X-ray diffraction experiment at 363 K revealed that not only the solvent molecules were removed, but also the rest of the inorganic cluster had transformed significantly from a butterfly shaped $[Zn_4(OH)_2]^{6+}$ to tetrahedral $[Zn_4O]^{6+}$ (Figure 1) due to an additional dehydration step ($2OH^- \rightarrow O^{2-} + H_2O$). Thus, instead of open metal sites, the coordination number of the zinc ions had changed. Variable temperature powder X-ray diffraction confirms the phase transformation occurs in the bulk. Gas sorption of CO_2, C_2H_4, and C_2H_6 succeeded on the transformed phase, which requires specific pre-treatment conditions.

A similar dehydration reaction occurs in the zirconium-based inorganic SBU of UiO-66 [1]. Rarely, has such a constitutional change been observed as directly as in this case and with as large structural rearrangement of the atoms in the SBU. Both clusters, $[Zn_4(OH)_2]^{6+}$ and $[Zn_4O]^{6+}$, are frequently observed in MOF structures (like MOF-5), and it stands to reason that the transformation observed here in the solid state can also occur in solution and determine the SBUs found in the product.

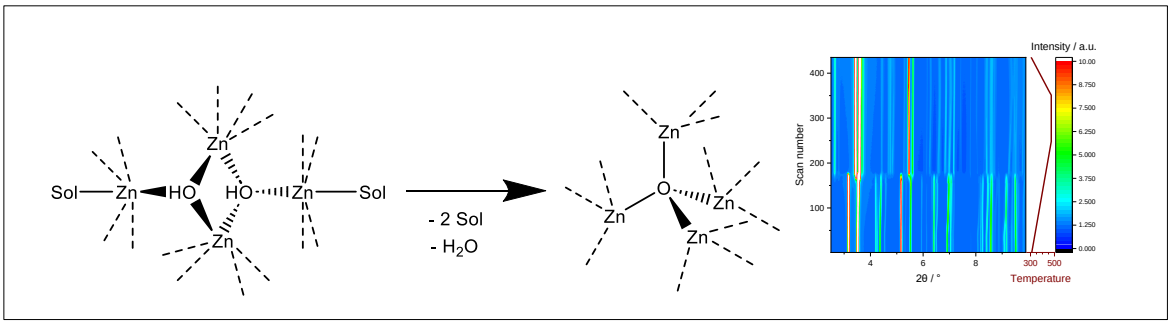

Fig.1. Left: Constitutional change of the inorganic SBU during desolvation and dehydration. Right: Observation of the phase transition in the variable temperature powder XRD pattern.

Funding

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Understanding the Microscopic Mechanism for the Industrially Relevant Ethylene/Ethane Separation by Silver-Containing Molecular Sieves

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A crucial step for the application of ethylene in derivatives is its separation/ purification from ethane molecules after being obtained by naphta or ethane steam cracking. The state of art method for such step is cryogenic distillation, currently one of the most energy consuming industrial processes[1].

Porous solids adsorbents are acknowledge as a highly promising alternative solution for this matter, which is the case of Metal Organic Frameworks (MOFs) and zeolites, for instance. Although some MOFs may present a rather poor stability[2], zeolites have been successfully used for industrial applications since the 1950's[3]. Another great advantage of zeolites is their tunability in terms of pore size, shape and surface functionality, allowing specific selective adsorption processes even at ambient temperatures. Due to the small differences of ethylene and ethane kinetic diameters (which is only 0.028nm) and their nearly identical physical properties, molecular sieving effect by itself is not effective enough for their separation. Therefore, this process must rely also on a Lewis acid-base interaction between the alkene and a transition metal cation, specially Cu(I) and Ag(I)[4,5], allocated in the adsorbent.

This study aims to comprehensively characterize the interactions between ethylene and Ag^+ exchanged zeolites, employing a multidisciplinary approach, combining Inelastic Neutron Scattering (INS), Infrared (IR) spectroscopy, Nuclear Magnetic Resonance (NMR), UV–Vis and Density Functional Theory (DFT) calculations[6]. CHA, RHO and LTA zeolites largely applied in gas separation processes, were chosen due to their similar small pore sizes and pore volume, but different cavity shapes and flexibilities. The interpretation of derived DFT Electron Density Difference, experimentally supported by ^{13}C Solid State NMR results, provide an understanding of each framework's role during the charge transfer mechanisms between ethylene and transition metal species. Specific deformations in the flexible framework of zeolite RHO explain a blueshift of the band at 400 cm^{-1} in the librational region of INS spectra compared to CHA and LTA. This structural change in RHO, represented by the conic shape of the cage 8-ring side pockets, increases steric effects over the adsorbate while rendering the metallic adsorption center less exposed within the zeolite's cavity, finally leading to a weaker adsorption energy. The redshift of C=C stretching frequencies observed by IR spectroscopy and DFT calculations, as well as C=C and C-H bond lengthening of ethylene confirm the formation of π-complexes on silver in the zeolites and allowed a further evaluation of the effects of the different frameworks cages on the aforementioned interaction.

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Assessment of Hydrophilicity/Hydrophobicity in Nanoporous Materials

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During the last decades, major progress has been made concerning the synthesis of nanoporous materials allowing for the custom design of nanoporous materials for targeted applications in various areas such as catalysis or separation. Enhancing the efficiency of these processes requires the tuning of the selectivity of the porous material to certain compounds of interest. Textural properties, such as the specific surface area and pore (entrance) size may affect the selectivity and transport properties and hence, the efficiency of the process. In addition to textural properties, the surface chemistry plays an important role since it can enhance the affinity and selectivity of certain compounds. The design and optimization of these processes therefore requires the detailed investigation of the relation between structural properties, surface chemistry and the resulting process performance.
Hence, reliable surface chemistry characterization of porous materials is essential for material development, product quality management as well as process development and optimization.To address this, we have developed a comprehensive strategy for assessing the surface chemistry of nanoporous materials by combining advanced adsorption studies, novel liquid intrusion techniques and NMR based techniques. [1-3] The developed advanced methodology allows for assessing the wetting behaviour of fluids on pore surfaces, i.e., in case of water the hydrophilicity/hydrophobicity of the pore surfaces over the whole range from complete wetting to non wetting adsorbates. We demonstrate this by utilising highly ordered SBA-15 silica (mode pore size ca. 6 nm) with tailored surface functionalization and more disordered, functionalised mesoporous silica utilised as stationary phase materials in chromatographic applications.

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Playing with thermodynamics and kinetics in CO_2 conversion catalysis

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The amount of CO_2 from the flue gas released by industrial processes and our activities is in the order of tens of gigatons globally. This enormous amount clearly points out that, besides actively demonstrated CO_2 sequestration technologies, we need to urgently develop highly efficient CO_2 conversion technologies to close the carbon cycle by recycling the carbon contained in CO_2 into a usable form. One of the most promising paths to valorise a great amount of captured CO_2 is its catalytic conversion to largely demanded chemicals like fuels. However, general challenges are its efficient activation and selective conversion to desired products. Numerous catalysts are developed to date; however, achieving high conversion efficiencies are often hindered by the high thermodynamic stability of CO_2 as well as by the unfavoured reaction kinetics and thermodynamics.
In this talk, chemical and engineering strategies for efficient catalytic conversion of CO_2 to chemical energy carriers are presented. Impacts of high-pressure conditions in combination with innovative catalysts on creating highly reactive environment will be presented for the synthesis of methanol, formates and CO among others. Furthermore, unique characteristics of unsteady-state operation to combine CO_2 capture and conversion in one process to produce syngas and methane are explained, highlighting the importance of *operando* methodologies to rationally develop and optimise catalytic materials and processes.

Sulfur Tolerance of Li-Ru/Al_2O_3 Dual Function Material for the Integrated CO_2 Capture and Methanation

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Carbon Capture and Utilization (CCU) is especially promising because it enables a net CO_2 consumption and at the same time the recycling of the carbon content of CO_2. A possible innovative solution to reduce the costs and increase the efficiency of the current multi-step CO_2 Capture and Utilization (CCU) processes is represented by the integration of the CO_2 capture and its hydrogenation into a single chemical looping process performed with Dual Function Materials. DFMs contain both a CO_2 adsorbent and a hydrogenation catalyst, which are intimately coupled and generally nanodispersed on a high surface area oxide support [1-4].

In this work we set out to investigate performance and durability of a Li-Ru/Al_2O_3 DFM during the integrated CO_2 Capture and Methanation (ICCM) in a fixed bed quartz reactor operated at atmospheric pressure and at a fixed temperature (from 260 to 320°C) with alternate feeds. We performed a prolonged ageing study under challenging feed conditions with a simulated flue gas containing 10-100 ppmv SO_2 in addition to H_2O and O_2. The Li-RuA DFM showed a remarkable sulfur tolerance during the cyclic operation at 280 °C preserving constant CO_2 conversion (≥90%) and CO selectivity (≥99.95%) (Fig.1). The DFM completely removed SO_2 storing it as lithium sulfate, which was stable during the subsequent hydrogenation stage, thus avoiding any severe poisoning of the catalytic Ru sites. However, the accumulation of sulfates progressively lowered the CO_2 capture capacity, and, in turn, the CH_4 production (Fig. 1), due to the saturation of the Li adsorption sites, which were not regenerated. The removal efficiency for SO_2 approached a breakthrough condition at ca 800 $\mu mol_{SO2}/g_{DFM}$: up to that point no H_2S was detected during the methanation stage.

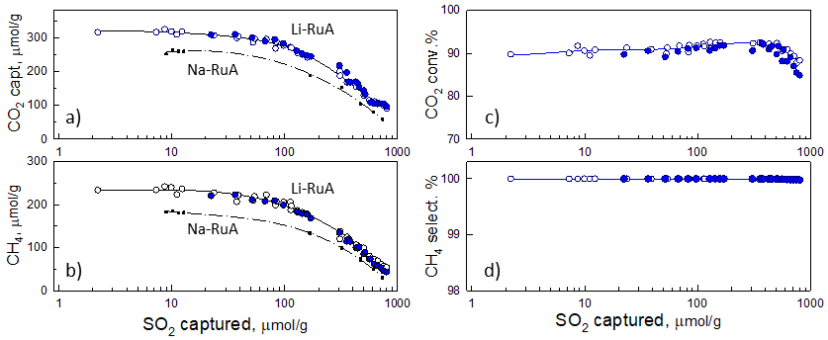

Fig. 1. ICCM on Li-RuA DFM at 280°C with a flue gas containing 5% CO_2, 1.5% H_2O, 0.25% O_2, and 10 or 100 ppmv SO_2 (open or closed symbols): (a) CO_2 captured, (b) CH_4 production, (c) CO_2 conversion, (d) CH_4 selectivity as a function of the cumulative amount of SO_2 retained on the DFM across cycles. Dash-dot lines correspond to data measured on a Na-RuA DFM [4].

Post-ageing characterization of the sulfurized DFM, after more than 100 cycles during 50 days at reaction temperatures, indicated a high stability of its textural properties and a limited increase of the average size of Ru nanoparticles due to sintering. Accordingly, the intrinsic methanation activity of the S-aged Li-Ru/A was comparable to the fresh unpromoted Ru catalyst. Notably, the high intrinsic catalytic activity of the Li-RuA DFM allows to optimally operate the process at temperatures as low as 260-280 °C, thus minimizing the potential poisoning effect of sulfur by preventing the formation of any RuS_x, because the catalytic assisted decomposition of Li-sulfates on the DFM is negligible below 280-290°C.

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Effetct of Pt load and Na addition to ZSM-5 for H_2 SCR of NO_x

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Introduction

Transports are responsible for a large fraction of CO_2 emissions and, in order to mitigate global warming, in addition to the development of electric cars, other solutions, still based on ICE, have been proposed, such as the use of hydrogen as a fuel. H_2 is virtually an emission-free fuel, but a completely NO_x free combustion cannot be ensured at all operating points [1]. A catalyzed exhaust after-treatment system with H_2 as a reducing agent would have the advantage that only one fuel needs to be carried on board both for propulsion and NO_x reduction, thus avoiding the device for storage and injection of urea, as for the more common NH_3-SCR.
The NO_x reduction by H_2 produces only elemental nitrogen and water:

$$2\ NO + 4\ H_2 + O_2 \rightarrow N_2 + 4\ H_2O \qquad (1)$$

MFI zeolite supported Pt catalysts exhibited higher N_2 selectivity than metal oxide supported catalysts, however, in the presence of excess O_2, typical of flue gases, Pt can easily catalyse NO oxidation to NO_2 [2, 3].In this work, the effect of Pt load at very low levels (0.1-1%) on the activity and selectivity and that of the addition of sodium to depress the oxidation activity of platinum have been investigated.

Results

The parent zeolite did not show any activity confirming the key role of the noble metal. The addition of an amount as low as 0.1%Pt promoted NO conversion to N_2 in the temperature range 80-200°C according to reaction (1). The temperature corresponding to the maximum NO conversion decreased with Pt load as well as NO conversion highlighting the effect of Pt dispersion. At T>200°C NO conversion is mostly associated with its oxidation with O_2 producing NO_2. The addition of sodium strongly inhibited the NO_2 formation at higher temperatures and also the N_2O production occurring simultaneously with reaction (1) (Fig.1). Catalysts were fully characterized (elemental analysis, XRD, porosimetric analysis, NH_3-TPD, in situ DRIFT) to determine the role of the support, of the Pt dispersion and of the acid properties on the catalytic performance.

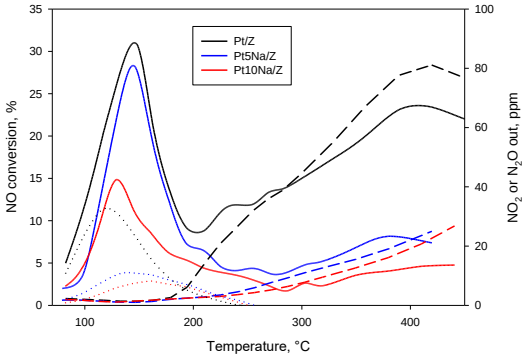

Fig. 1. NO conversion (solid line) and outlet concentration of NO_2 (dashed line) and N_2O (dotted line) of Pt/Z, Pt5Na/Z and Pt10Na/Z.

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Nitroarene Hydrogenation Using Nitrogen and Phosphorus Co-doped Activated Carbon

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Carbon-based metal-free catalysts, such as doped activated carbons, have gained interest for nitroarenes' sustainable, cost-effective, and non-toxic hydrogenation [1]. This interest stems from the ability to easily control fundamental properties like porosity and surface chemistry, which are essential for catalyst design [2]. While various heteroatoms such as nitrogen (N), phosphorus (P), and boron (B) have demonstrated promising activity in doped carbons, the cooperative effects of co-doping remain relatively underexplored, especially in the context of nitroarene metal-free catalysis using activated carbons [2]. This study aims to produce substituted anilines using N, P-doped activated carbon. A commercial activated carbon (RGC-30) was modified with melamine (Mel) and phytic acid (PA) as sources of N and P, respectively (MelPhy). Initially, RGC-30 was treated with Mel, followed by treatment with PA at various temperatures and mass ratios. Additionally, mono-doped carbons were synthesized with N (RMel) and P (RPhy) doping for comparative analysis. Catalytic tests revealed that simultaneous N- and P-doping resulted in higher catalytic activity than their mono-doped counterparts (Figure 1). Furthermore, ICP-MS and XPS data indicated that using N-doped carbons as the base material for P introduction when PA was the doping agent led to higher incorporation of phosphorus groups compared to P-doping with unmodified carbon. These catalysts demonstrated robust activity, high selectivity, and considerable stability, with enhanced catalytic performance observed after multiple recycling cycles due to surface modification.

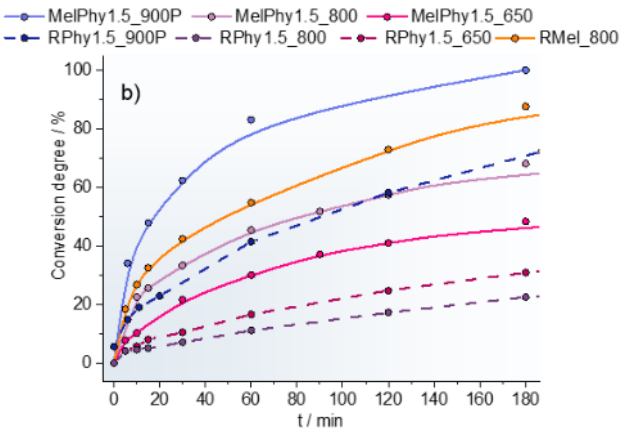

Fig.1. Catalytic result for the hydrogenation of 1-chloro-4-nitrobenzene using N, P-doped carbons. T=80ºC, 5 mmol substrate, 100 mg catalyst.

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Influence of Heteroatom Doping on Heterogeneous Cobalt Catalysts for the One-Pot Synthesis of Benzimidazoles by Reductive Coupling of Dinitroarenes with Aldehydes in Water

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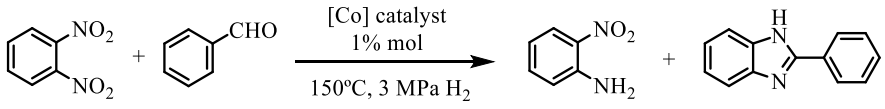
The development of active and selective non-noble metal-based catalysts for the chemoselective reduction of nitrocompounds able to work in aquo media under mild conditions is an attractive research area. In fact, this reaction is key in the synthesis of derived products such as benzimidazoles, which are molecules of significant industrial interest in drug development, agriculture and material science. [1] The primary challenge in their synthesis lies in the requirement for an extremely acidic reaction medium, the employment of toxic solvents and the use of noble metal as catalyst. [2] Herein, the synthesis of a family of cobalt catalyst doped with N and P for the direct synthesis of benzimidazoles by means of reductive amination of dinitroarenes is presented. For that purpose, we investigated the use of N and P heteroatom-containing ligands as precursors for synthesizing durable carbon-supported nanoparticles. All catalysts synthesized in this work were exhaustively characterized by several advanced techniques such as X-ray fluorescence (FRX), X-ray diffraction (PXRD), X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS) and high-resolution transmission electron microscopy (HRTEM) to better understand the cobalt species' nature.

These as-prepared catalysts showed high activity, chemoselectivity and stability toward the reductive coupling of dinitroarenes and aldehydes with H_2 under mild reaction conditions and water as a green solvent, improving the only two reported results based on Mo and Au in non-green conditions. In this work, we demonstrate how the effect of phosphorous and nitrogen in cobalt nanoparticles improves the production of benzimidazoles in the mildest conditions reported up to date (**Table 1**).

Table 1. Catalytic results in the synthesis of benzimidazoles with 1,2-dinitrobenzene as substrate



1a **2a** **3a** **4a**

Catalyst	Conversion (%)	Selectivity to 3a (%)	Selectivity to 4a (%)
Co@C	97	97	0
Co_2P@C	90	88	2
CoN_x@NC	>99	62	37
Co_2PN_x@NC	>99	0	>99

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Methane pyrolysis: Unlocking the potential for COx-free Hydrogen Production

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The rapid technological development and the overpopulation intensify the global energy demands. Although the developed technologies, market structures and scientific knowledge depend on fossil fuel energy, the climate change and the energy crisis make the need for decarbonization of the global economy urgent [1-2]. Hydrogen (H_2) is considered to be one of the most promising energy carriers and clean fuels, since it has considerable energy density and its combustion implies zero carbon emissions. Among the H_2 production methods, methane pyrolysis poses a sustainable solution for COx-free hydrogen production, as the co-products are only solid carbon allotropies. However, methane pyrolysis requires high temperatures and the solid allotropies are often amorphous carbon. For that reason, research has been dedicated to catalyst development, in order to decrease the temperature regimes [3] and selectively produce valuable carbon structures, which have the potential to be used in a vast number of applications, such as batteries, or as automotive parts, additives etc. It is easily understood that the cost of the procedure is highly correlated to the valorisation of carbon products [1]. Regarding the sustainability of the method, recent techno-economic assessments indicate that H_2 production by this developing technology has similar cost with the already developed steam methane reforming, since the latter method produces high amounts of CO_2, requiring an extra step of carbon capture [1-2]. Furthermore, when methane pyrolysis is compared with eco-friendly water electrolysis, it theoretically consumes 37.425 kJ to produce 1 mol of H_2, while the energy input of water electrolysis is as high as 285.6 kJ [2]. As a conclusion, the continuous development of catalytic methane decomposition provides high-value carbon materials, which significantly decrease cost of H_2 production and encourages for future transition to large scale H_2 and graphitic carbon utilization [1]. The catalytic materials are either solid or molten. Although in the case of molten catalysts, carbon is separated more easily from the molten media, the procedure requires temperatures higher than 1000^o C. On the contrary, regarding the solid catalysts, the materials that are mostly selected include inexpensive transition metals such as Ni, Co or Fe because they are sufficiently active and stable at much lower temperatures [3].

The aim of our current studies [4] was to synthesize novel (5wt%) Fe- or Co-based solid catalysts on alumina support carrier and investigate the effect of synthesis method and the impact of incorporating small amounts (0.5wt%) of a noble metal, such as Pd. The selected synthesis methods were Wetness (WI) or Spray impregnation (SI) of the metals on the support. It was evidenced that WI offers a uniform distribution of the metals on the support, while the SI approach creates core-shell structures, which were proved to promote the catalytic activity of all samples and enhance the deposition of more graphitic carbon. Moreover, the Fe-catalysts showed higher conversion rates than the Co samples. Incorporation of Pd on both Fe-alumina and Co-alumina samples, was beneficial both for the catalytic activity and the carbon nanofiber production. More specifically, the Pd-doped Co catalysts outperformed the Pd-doped Fe catalysts, so the spray impregnated Pd-Co/alumina sample was selected to further investigate the catalyst performance under 8 hours of CH_4 pyrolysis reaction. The initial catalytic decomposition of methane was ~78% and gradually decreased to 29% after 8h. It is worth mentioning that the reaction was selective towards H_2 production and the increase of the reaction time promoted the increase of size and quantity of carbon nanofibers. Higher (10%) Co loading significantly enhanced initial catalytic activity, while bimetallic Co-Fe exhibited additional stability outperforming the Pd-Co/alumina sample.

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Visible light assisted CO_2 valorization to CO over metal@oxide semiconductor photocatalysts

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Photo-thermal reduction of CO_2 into methane, methanol and carbon monoxide over suitable (photo)catalysts is a feasible pathway for producing fuels and chemicals with minimal involvement of fossil fuels. Illumination of the catalyst enables non-thermal energy input in the form of hot carriers (electrons and holes), as well as strongly enhanced electromagnetic fields at the plasmonic metal nanoparticles, leading to deposition of rotational and vibrational energy into surface adsorbed species. Consequently, reaction rates can be significantly accelerated, selectivity of the reaction can be steered and conversions beyond the thermodynamic equilibrium can be achieved.

The approach of our research team to visible light assisted catalysis is: (i) first focusing on the presence of active sites that enable the catalytic reaction that is being analyzed and (ii) secondly, presence of light absorbing components. We are also capitalizing on oxygen deficiency and defect generation in the oxide semiconductors like CeO_2, TiO_2 and WO_3 under reaction conditions, which makes them efficient visible light absorbers, Fig. 1 [1,2].

This lecture will focus on light-assisted CO_2 to CO conversion using methane or H_2 as reducing agents via methane dry reforming and RWGS reaction pathways using Ni/CeO_2 and $CuZnAlO_x$ catalysts. I will also provide an example of how and more importantly, why one seemingly very promising photo-catalyst fails to provide any activity for (photo)thermal CO_2 hydrogenation.

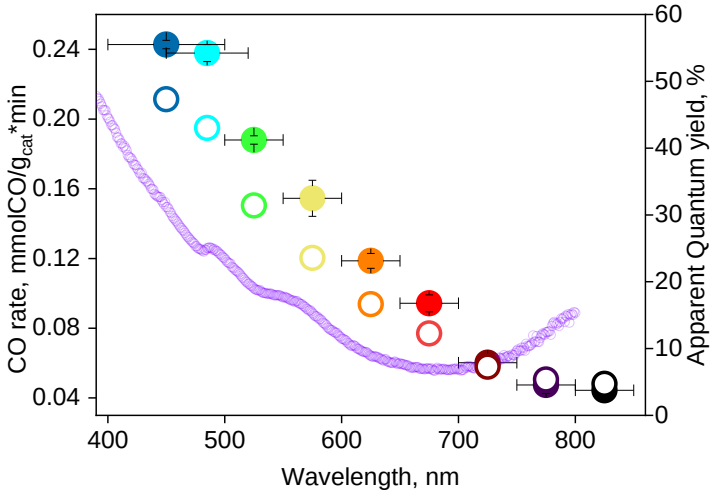

***Fig. 1**. Wavelength dependent CO rate during light assisted RWGS reaction over $CuZnAlO_x$ catalyst (full symbols) and AQY using irradiance of 12.7 W/cm^2 (empty symbols). Purple trace shows UV-Vis absorbance recorded in-situ under reaction conditions (T= 230°C, CO_2=H_2= 15ml/min).*

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Electrocatalysis Under Confinement: CO_2-Reduction with Molecular Catalysts Immobilized on Ordered Mesoporous Carbons

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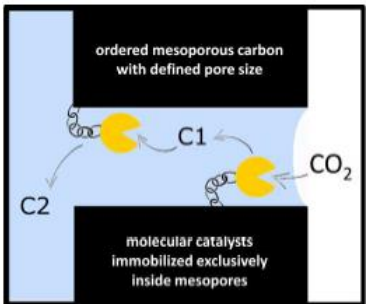
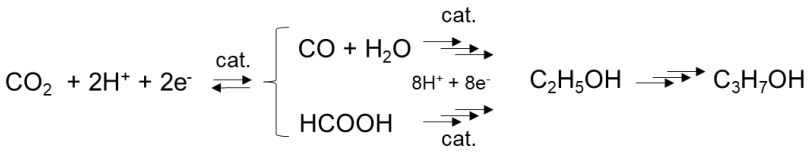
The goal of this work is to investigate confinement effects and maximize activity and selectivity for the formation of C2+ products using molecular catalysts tethered inside the pores of ordered mesoporous carbons (OMCs). Three primary confinement effects are studied:
1. Amplification of Intermediate Concentration: Confined geometries enable further electron and proton transfers beyond the 2-electron reduction products CO and HCOOH (formic acid).
2. CO_2 "Over Solubility" in Confined Geometries: Gas solubility increases in liquids confined within mesopores compared to bulk liquid.
3. Electrical Field Effects in Nanoconfined Electrolytes: Changes in the electrical double layer and potential decay occur in the radial direction of the pores.

Metal porphyrinoid catalysts like iron porphyrin (Fe-por) and cobalt corrole (Co-cor) tethered inside OMC pores will be used to study and utilize confinement effects, focusing on intermediate amplification to control the product spectrum. Our study compares the performance of Fe-porphyrin as a molecular catalyst within OMC pores versus dissolved in electrolyte. Using an H-type cell setup, we investigated how this configuration impacts the electrochemical CO_2 reduction reaction (CO_2RR), emphasizing confinement engineering and tethered molecular catalysts in OMCs.





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Surface Chemistry and Photodegradation: Insights into Heteroatom-Mediated Catalysis

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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. In this context, carbon-TiO_2 composites are the go-to basis for validating their true ability to improve their photocatalytic performance. Our investigation focused on modulating carbon nanotubes with oxygen, nitrogen, or phosphorous, enriching P25 through meticulously tailored chemical pathways and wet impregnation with methanol. 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 suggestive of enhanced electron-hole mobility at the nanotube/TiO_2 interface, especially for TiO_2/OSWCNT and TiO_2/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 aimed at enhancing photocatalytic activity in oxidation reactions toward a cleaner future.

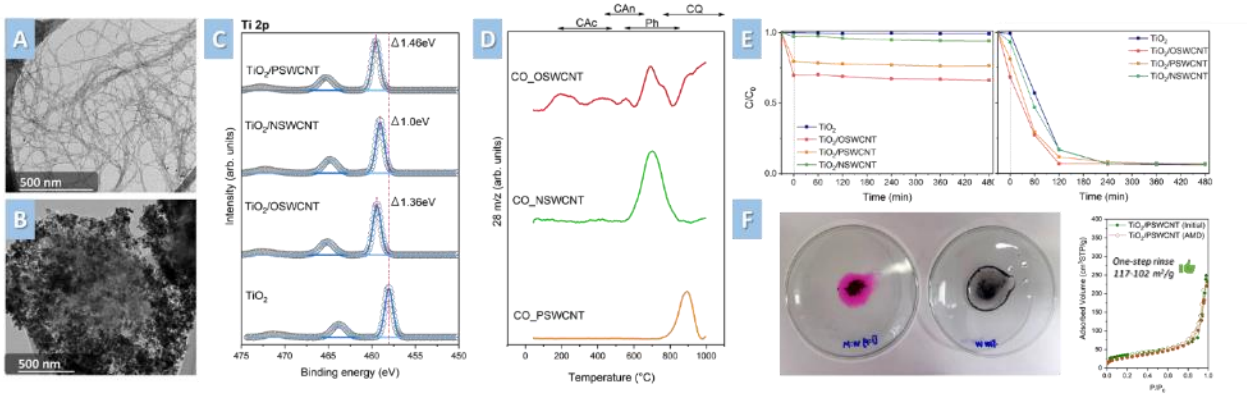

Figure 1. Highlights of the catalyst's physicochemical characterization and photocatalytic performance.

Acknowledgments

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Photocatalytic conversion of CO_2 to methanol using copper oxide and vanadium oxide co-deposited on titania nanotubes

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Since the Industrial Revolution, the emission of greenhouse gases like CO_2 has accelerated global warming, posing significant threats to society and the environment. A promising solution is the conversion of emitted CO_2 into methanol using photocatalysts such as titanium dioxide (TiO_2) and water as co-reactant. However, TiO_2-based materials face challenges in absorbing visible light, utilizing only 5% of the solar spectrum. In this reserach, copper oxide and vanadium oxide co-deposited on titania nanotubes (Cu_xO,V_xO_y-TNT), active under simulated solar light, were synthesized by electrochemical and wet chemical techniques. The photocatalysts were characterized using several experimental methods and investigated for the photocatalytic conversion of CO_2 and water vapor to CH_3OH.

Results indicate that metal oxide deposition was successful via wet impregnation, but not through the electrochemical method. Additionally, the Cu_xO,V_xO_y-TNT sample achieved a methanol yield of 0.220 µmol g^{-1} h^{-1} cm^{-2}, which is 10 times higher than the yield reported in a similar study by *D. Guisi et al.* [1]. Compared to samples deposited with only one metal oxide (Cu_xO-TNT and V_xO_y-TNT), the co-deposited sample exhibited the highest selectivity towards methanol production at 7.60% (**Fig.1.**).

The improved photocatalytic performance of the co-deposited sample can be attributed to the extension of visible light absorption by V_xO_y, enhanced selectivity towards methanol production by Cu_xO, increased surface area in TNTs for CO_2 adsorption, and reduced charge recombination likely due to Z-scheme formation. Our results suggest that co-depositing nanostructured photocatalysts significantly enhances their textural and photocatalytic properties, marking a step forward in sustainable technology.

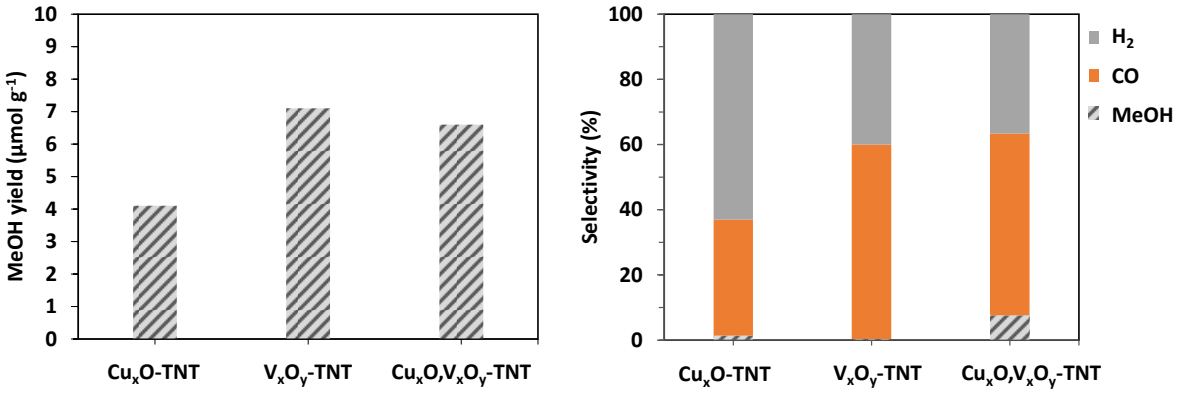

Fig.1. Methanol yield (µmol g^{-1}) and product selectivity (%) from the photocatalytic conversion of CO_2 after 5 h irradiation.

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Nanoporous Materials for Fenton-like and Photo-Fenton-like Water Cleaning via Heterogeneous Catalysis

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Over recent decades, water pollution from organic contaminants of emerging concern (CECs) has become a significant issue. Among various treatment methods, advanced oxidation processes (AOPs) have gained prominence. These processes generate highly reactive oxygen species that can indiscriminately break down organic pollutants into environmentally benign byproducts like H_2O, CO_2, and inorganic minerals. Fenton AOP is one of the most applicable AOPs. The Fenton reaction utilizes iron salts (Fenton reagent) as homogeneous catalysts in the presence of hydrogen peroxide (oxidant). This method is well-studied for its effectiveness, environmental friendliness, and economic feasibility. However, traditional Fenton processes have limitations, such as the need for specific acidic conditions (optimal pH 2.8–3.5), significant iron sludge production, and the necessity for post-treatment to manage excess iron ions in water effluents. To address these drawbacks, employing Fenton-like reactions at neutral pH using heterogeneous catalytic systems has been proposed. Additionally, the photo-Fenton approach shows promise by combining photocatalytic reactions to produce •OH via above-bandgap excitation of certain photocatalysts.

In this lecture, we demonstrate that tailoring the morphology and optimizing the metal concentration in multicomponent nanoporous catalysts through appropriate synthetic strategies can lead to efficient Fenton-like and photo-Fenton-like heterogeneous catalytic systems. [1-3] These systems are capable of effectively degrading bisphenol A and coumarin as model CECs, with coumarin also serving as a probe for •OH detection.

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Green Fabrication of Carbon-Coated Macrostructured Catalysts with Sodium Alginate Assistance

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Carbon based materials coatings have an important role in catalysis processes. Their immobilization in structured supports emerges as a key-step that contributes to the safe application in several catalytic reactions [1,2]. The use of synthetic surfactants to promote carbon nanotubes (CNTs) dispersion, although very promising, may result in environmental damage since they are toxic to aquatic life with long lasting effects even if they are removed during the catalyst preparation [3]. The study and development of more efficient alternatives for materials dispersion to effectively immobilize different types of carbon-based powder materials emerge as an urgent need to mitigate these risks.
A novel and environmentally friendly synthesis methodology for carbon-coated macrostructured catalysts was developed using sodium alginate (SA) as a dispersant to ensure the proper dispersion of modified CNTs. A comprehensive study of the synthesis methodology and optimal coating conditions was performed in order to produce active and stable carbon-coated macrostructured catalysts. The dispersant decomposition proved to be a key-step to promote the catalyst stability, which was achieved by a thermal treatment process at 550 ºC (sample WCP_{SA}_550). The catalytic activity of these catalysts was tested for the catalytic ozonation of oxalic acid (OXL), a refractory model organic pollutant, and the obtained results showed a degradation of around 75 % (results present in Fig. 1), which was superior when compared with the results obtained with carbon-coated macrostructured catalysts synthesized using more conventional methodologies. The developed methodology proved to be highly versatile, allowing for the easy immobilization of different carbon-based materials (such as composites).

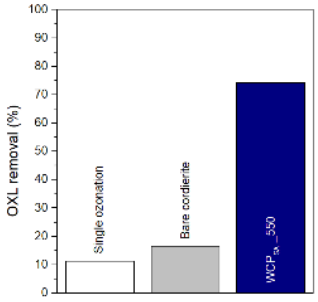

Fig. 1. Oxalic acid removal through catalytic ozonation.

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Empowering the gas desulfurization efficiency of carbon materials through incorporating active inorganic phases

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Hydrogen sulfide (H_2S) 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 H_2S 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 H_2S 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 H_2S removal up to 387 mg/g.

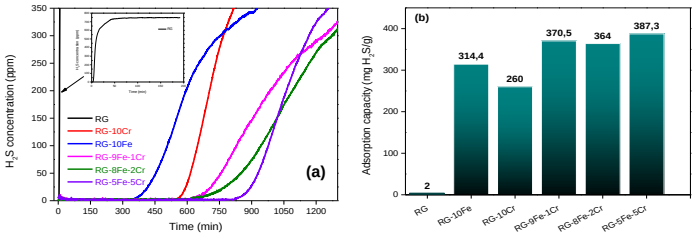

Fig.1. The breakthrough curves (a) and H_2S removal capacity (b) of the prepared adsorbents.

Acknowledgements

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Gas-phase simulated moving bed for methane and nitrogen separation using maxsorb extrudates

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Due to the depletion of conventional natural gas wells, unconventional methane-rich sources have been increasingly explored. These sources often contain impurities, notably nitrogen, which is difficult to remove because of the similar properties of nitrogen and methane. To meet pipeline specifications, nitrogen content must be reduced to below 3% to maintain the calorific value of the stream [1]. The main technology used for this purpose is cryogenic distillation, which has very high energy costs associated and is unsuitable for medium and small-scale purification of methane streams [2]. When compared to this technology, adsorption-based processes are very appealing due to their easy scalability and lower energy requirements. However, the adsorbent performance for CH_4/N_2 separation may be an issue due to their low selectivity [3]. Using a gas-phase simulated moving bed (SMB) process overcomes this challenge since it can separate mixtures with an adsorption selectivity close to unity.

For the design and development of a gas-SMB process, firstly, pure component isotherms of N_2, CH_4, Ar, and CO_2 were measured at 303, 323, and 343 K in a pressure range of 0 - 2.5 bar using a volumetric apparatus. The data was successfully regressed with the single-site Langmuir model. The results showed that CO_2 has the highest affinity to the stationary phase and Ar the lowest over the studied temperature and pressure range.

Single, binary, and ternary breakthrough experiments were conducted at 303 K and 1.5 bar, with a total flow rate of 0.2 SLPM. A mathematical model that encompasses mass, energy, and momentum balances was implemented in the gPROMS® software and utilised to predict the observed adsorption dynamics [4]. The ternary experiments have shown that the desorbent is easily displaced by the mixture and can equally displace the adsorbed phase, which is an essential step for SMB operation.

Finally, two simulated moving bed (SMB) cycles were employed to separate an equimolar CH_4/N_2 mixture using each desorbent gas to evaluate the desorbent strength's impact in the process. The desorbent-free purity for both cycles was very high (100% and 99.3% for the Argon and CO_2 experiments, respectively). Both cases also achieved a high recovery (> 97%). When argon was used as the desorbent gas, the extract product stream was obtained with a productivity of 14.3 $kg \cdot m^{-3}_{ads} \cdot h^{-1}$.

Acknowledgements

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Grignard Surface Modification: Insights Into The Modification Mechanism And Surface Properties

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Metal Oxides like Titania have shown profound applications in separation technology, such as in sorption and membrane processes[1]. The applicability of these metal oxide membranes are limited due to the presence of hydroxyl surface sites, making the membrane hydrophilic and limiting specific surface interactions that are needed to introduce affinity separation capabilities. To avoid these issues, metal oxides can be modified with organic groups, introducing hydrophobicity to their surface and specific interactions from a wide diversity of organic (functional) groups. These organic grafted metal oxides, known as Organic-Inorganic hybrids, can exhibit synergic properties and provide unique applications. One such interesting surface modification involves using Grignard reagents on titania[2].
The organic groups are introduced to the surface of the Titania via reaction with Grignard reagents, resulting in compatibility with a wide range of solvents, needed for organic solvent nanofiltration[1] as well as anti-fouling properties[3]. However, the mechanism of Grignard grafting remains elusive and complex, as there's a noticeable reduction process involved (evidenced by a color change of powder in solution after addition of Grignard reagent). The current work focusses on organic grafting on titania using various Grignard reagents such as ethyl and octyl magnesium chlorides, phenyl magnesium bromide and others. Hence, the goal is to study the reduction behavior of titania during Grignard modification and its correlation with the modification degree (using EPR, TGA-MS, IR and XPS measurements), and to study the influence of crystal phases and facets on the modification process (using phase pure titania powders).

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Analysis of the flowrate effect on the continuous adsorption of diclofenac using carbon nanotubes functionalized with Fe nanoparticles

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This project studied the green functionalization of CNTs utilizing coffee husks to impregnate iron nanoparticles on the surface of the material. Furthermore, the continuous fixed-bed adsorption of diclofenac sodium was investigated, specifically analysing the effect of the feed flow rate on the system. Pre-functionalized multi-walled carbon nanotubes with OH and COOH groups (functionalization degree = ± 9%) were used. The functionalization with iron nanoparticles followed the green route methodology adapted by the research group, using coffee husks as reducing agent for the deposition of iron nanoparticles in the CNTs surface [2, 3]. The CNTs (0.1 g) were immobilized in the fixed bed column (1 cm diameter, 10 cm height) using treated sand (10 g). The efficiency parameters evaluated were the adsorptive capacity until rupture (q_r), adsorption capacity at saturation (q_s), length of the mass transfer zone (MZT) and percentages of removal at rupture (%R_r) and saturation (%R_s).

Figure 1 and Table 1 show that the flow rate of 0.2 mL.min^{-1} was the most effective, as indicated by the prolonged time to reach the breakthrough point. This longer contact time with the adsorbent promoted greater removal due to interactions between the molecules and the functional groups on the CNT surface. Additionally, the lower flow rate resulted in the highest removal percentages up to the breakthrough and exhaustion points. Despite the highest value for the mass transfer zone, low variations were observed in this parameter under other conditions (±0.174 cm). However, at this flow rate, the time to reach column saturation was the longest (3600 min), and total saturation was not achieved (C/C_0 = 0.88). The system at a flow rate of 0.4 mL.min^{-1} had a shorter breakthrough time, but the efficiency parameters were very close to those of 0.2 mL.min^{-1}, making it potentially more suitable depending on the desired application.

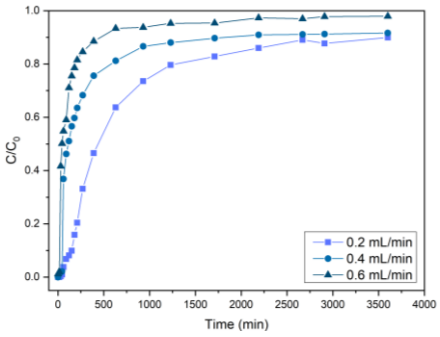

Fig.1. Breakthrough curve of the dynamic study at the initial DS concentration of 0.2 mmol.L^{-1}.

Table 1. Efficiency and mass transfer parameters from the fluid dynamic study.

Feed flow rate (mL.min^{-1})	t_r (min)	t_s (min)	q_r (mmol.g^{-1})	q_s (mmol.g^{-1})	MZT (cm)	%R_r	%R_e
0.2	71.975	3600	0.024	0.308	9.21	100.00	25.28
0.4	46.216	2190	0.033	0.309	8.94	96.39	19.12
0.6	16.122	630	0.016	0.147	8.88	92.13	21.12

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FAPESP (Grant #2020/16004-9), CNPq (Grants # 406193/2018-5 and #308046/2019-6) and CAPES (Finance Code 001).

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Synthesis of graphene oxide and clay-based nanocomposite for adsorption of emerging pharmaceutical contaminants in water

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Among the various emerging pollutants in water, medicines represent the most significant category due to the use of many therapeutical agents, such as antibiotics, anti-inflammatories, and analgesics. Even at minimal concentrations they pose potential risks to aquatic organisms and human health. Nevertheless, removing these compounds from water using traditional treatment methods is challenging. Among the pharmaceuticals, propranolol, chloroquine and caffeine stand out. Propranolol is widely marketed for the treatment of high blood pressure and other associated diseases, and this is in line with its high consumption rate [1]. Chloroquine was developed in 1930, having proven efficacy against malaria. However, despite being proven not to be effective for COVID-19, it was proposed as a medication in some countries, such as Brazil [2]. It is estimated that during the first 15 months of the COVID-19 pandemic, its consumption in Brazil increased by 167%. Another emerging contaminant present in various foods such as coffee, tea, beverages, and medicines is caffeine, which is considered an indicator of human contamination. Its presence has been widely detected in aquatic systems around the world [3, 4]. Consequently, the development of new technologies and materials for removing these contaminants is necessary. Among the options, adsorption can be identified as a viable technology for removing organic compounds [2]. Nanostructured adsorbents have demonstrated good efficiency in water treatment due to their extensive surface area and potential for regeneration and reuse. This work aims to produce and apply a graphene oxide (GO) and green clay (montmorillonite) nanocomposite as adsorbent for chloroquine, propranolol and caffeine removal from water. Considering the extensive theoretical surface area of GO, the idea is that the combination of GO with clay will significantly improve the material's adsorption capacity for contaminants in water, facilitating the separation between adsorbent and adsorbate later. GO was synthesized through graphite chemical oxidation, following a modified version of the Hummers method. The nanocomposite synthesis occurred via precipitation in a ratio of GO 1:6 green clay, where the clay was added slowly under stirring. After 30 min, the suspension was transferred to a sonication bath for another 30 min. Then, HCl was added dropwise under gentle magnetic stirring until pH=2. A brown composite was formed and precipitated. The solid phase was collected by vacuum filtration and washed in deionized water [5]. The synthesized material was calcined in a muffle furnace for 4 h at 300°C. Preliminary adsorption tests were carried out for each contaminant, using 0.10 g of the nanocomposite in 25 mL of the respective pharmaceutical solution, at 20 $mg.L^{-1}$ initial concentration, 25ºC and 24 h of contact. Results obtained showed removal efficiencies >99% (99.87% for chloroquine, 99.45% for propranolol, 99.58% for caffeine). However, scanning electron microscopy (SEM) analyses will be performed for the nanocomposite before and after adsorption.

Funding

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3D-printed Hybrid Monolith for CO_2 Capture

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The Intergovernmental Panel on Climate Change (IPCC) reports that Europe's climate is changing due to global warming, rising temperatures and changing precipitation patterns. Reducing carbon dioxide (CO_2) emissions is essential to mitigating climate change, and power plants are among the largest CO_2 producers. Carbon capture and storage (CCS) is an effective method to reduce CO_2 emissions from these plants, with adsorption-based techniques being a viable approach.
To ensure efficient adsorption processes, optimising the properties of the adsorbents is crucial. Traditional packed beds with pellets or beads are commonly used in industries. However, these structured adsorbents have drawbacks, such as high pressure drops and attrition. Additive manufacturing (AM), also known as 3D printing, offers an alternative approach to developing structured adsorbents suitable for large-scale applications. Although promising, shaping adsorbent materials using AM technologies requires further exploration.
In this study, an adsorbent monolith composed of 50% zeolite 13X and 50% activated carbon using direct ink writing was developed. The effects of shaping this structured adsorbent for CO_2 capture on its characteristics and mechanical strength were analysed to assess its suitability for large-scale applications. The material was characterised using nitrogen (N_2) physisorption at 77 K, CO_2 adsorption at 273 K, mercury porosimetry, and crushing tests.
Additionally, pure CO_2 and N_2 adsorption equilibrium isotherms at 303, 333, and 373 K, within pressure ranges of 0 to 1.5 bar for CO_2 and 0 to 5 bar for N_2, were measured. The Dual-Site Langmuir model described the isotherms well, with CO_2 exhibiting a higher affinity for the 3D-printed monolith. At a CO_2 molar fraction of 0.15, under 1 bar and 303 K, the selectivity of the monolith is 30.7.
Dynamic adsorption experiments were conducted with and without electric current assistance for material regeneration. A mathematical model was employed to describe the breakthrough curves. During the adsorption step, a compressive CO_2 mass front is observed, while a dispersive mass front appears during the regeneration step, consistent with the behaviour of the measured isotherms. Desorption was more rapid when the adsorbent material was electrified.

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Mechanochemistry and ZIFs; facile functionalisation of porous frameworks for CO_2 capture

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Mechanochemistry has in recent years shown to be a reliable and fast synthesis method for synthesis of various MOFs and ZIFs. Despite a multitude of papers on mechanochemical preparation of ZIFs the scope of mechanochemically prepared frameworks is limited to a scant few. Herein we report on a series of functionalised sodalite ZIFs, prepared through either direct synthesis (Fig.1 left) or post-synthetic linker exchange using mechanochemistry (Fig.1 right). The prepared ZIFs were then evaluated for their potential as CO_2 sorbents (Fig.1) compared to the benchmark ZIF-8.

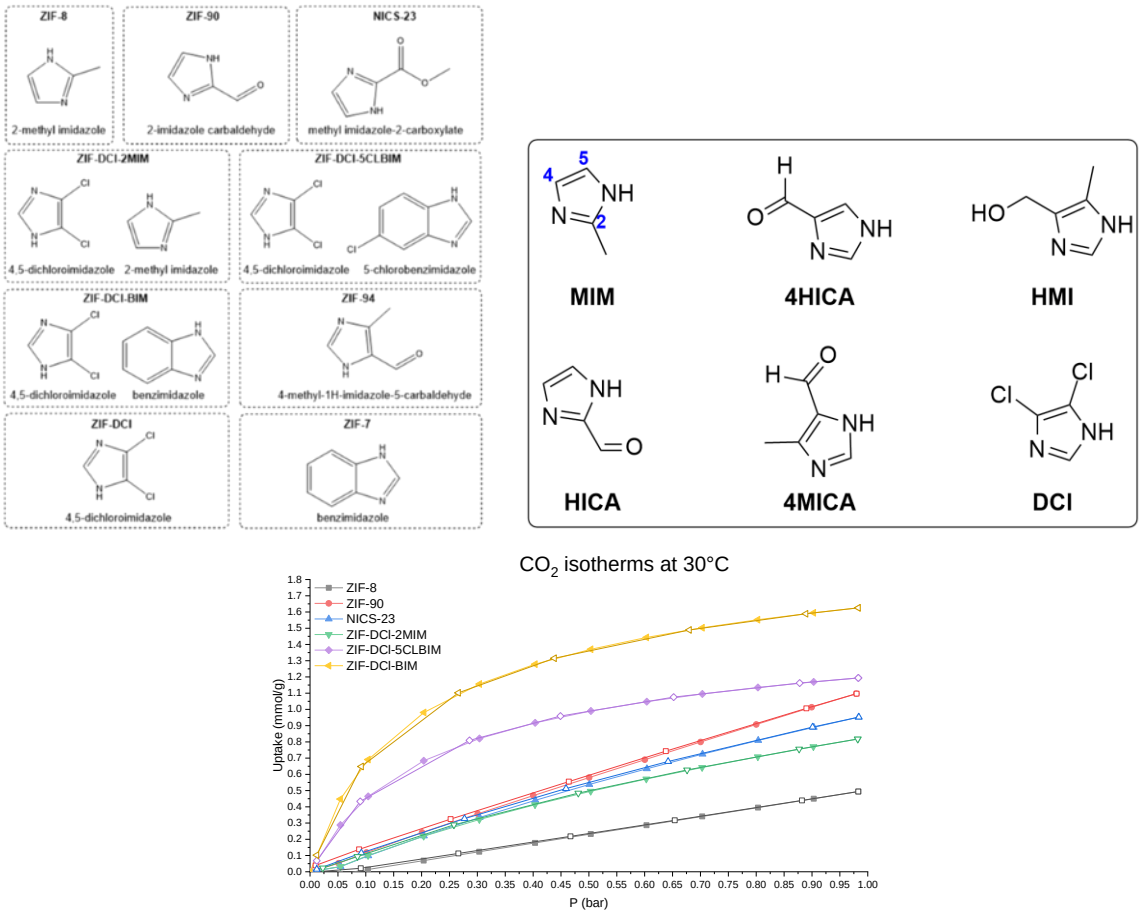

Fig. 1. top left: ZIFs directly synthesised top right: linkers used for mechanochemical ligand exchange. Bottom: CO_2 isotherms of the synthesized samples.

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Novel microporous zinc-based MOF for selective CO_2 capture

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Metal-Organic Frameworks (MOFs) are a class of porous crystalline materials known for their unique chemical and physical properties, which make them suitable for numerous applications. Recently, MOFs have become a promising solution for selective CO_2 capture and separation [1,2]. Due to their well-regulated structure, large surface area, and adjustable porosity, MOFs can be tailored to have a higher affinity for CO_2 [3].

One MOF that has received significant attention is the Calgary Framework-20 (CALF-20) [4]. This framework consists of layers of 1,2,4-triazolate-bridged zinc(II) ions, pillared by oxalate ions. CALF-20 is one of the few MOFs to be used at the industrial scale. Its high water resistance and strong CO_2 affinity have led to its deployment in a large-scale CO_2 capture facility at a cement production plant, effectively capturing up to 1 tonne of CO_2 per day since 2021.

To enhance CO_2 capture, one strategy is to functionalize the framework by adding additional functional groups to the structure. This incorporation of more active sites within the MOF allows for greater interaction with CO_2 molecules. A CALF-20-like framework with an additional amino functional group on the triazolate linker, known as CALF-15, has been reported in the literature [5,6]. Inspired by this, we aimed to incorporate an additional amino functional group into the framework, resulting in a new MOF structure named NICS-24 (**Fig.1**).

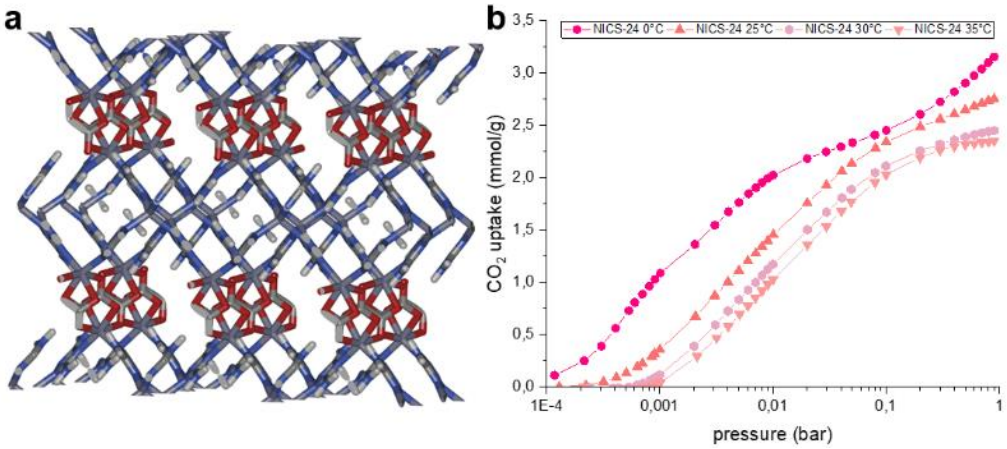

Fig.1. (**a**) Visualization of the NICS-24 structure, (**b**) equilibrium adsorption isotherms for CO_2 up to 1 bar for NICS-24 at different temperatures.

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Hydrogenation of CO_2 to hydrocarbons with multimetallic carbon catalysts

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Carbon dioxide (CO_2) is the most common greenhouse gas, accounting for about 81 % of these gases. The increase in these emissions results in global warming, which triggers climate change and has consequences such as fresh water shortages, rising floods and rising sea levels, which influence livestock, agriculture, and the global food system [1].

The catalytic hydrogenation of CO_2 has shown to be a promising technology for valuing this pollutant. While notable advances have been made in converting CO_2 to products containing just one carbon atom (C_1), the hydrogenation of CO_2 to products with 2 or more carbon atoms (C_{2+}) presents additional challenges due to the inertness of CO_2, but it of greater economic and environmental interest [2].

The main objective of this work was to study the performance of multimetallic catalysts supported on carbon nanotubes in the hydrogenation of CO_2 to hydrocarbons (C_2-C_4) through modified Fischer-Tropsch synthesis (FTS).

The impregnated metals were Fe, Cu, Na and K, with the reaction taking place in a Microactivity-Reference (PID) reactor. The analysis of the reaction products was carried out on a Micro GC Fusion Gas Analyzer chromatograph. All catalysts were evaluated under a flow rate of 50 vol.% H_2 + 16.7 vol.% CO_2 + 33.3 vol.% N_2 (30 cm^3 min^{-1}), pressure of 15 bar and temperature of 350 ºC.

The catalyst that demonstrated the best performance in the hydrogenation of CO_2 to C_2 - C_4 hydrocarbons was FeCu_CNT, with CO_2 conversion of 50% and selectivity to C_2 - C_4 of 49 %. Fe plays a critical role since in the catalyst synthesized only with Cu, Cu_CNT, the CO_2 conversion is only 20 %, and the selectivity to the intended products is 4%. The addition of Na and K to the catalyst causes a decrease in selectivity to products C_2 to C_4 due to the increase in selectivity to the most common secondary products of the reaction under study, CO and H_2O.

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Innovative carbon:Al_2O_3 composite support for catalysts to CO_2 Hydrogenation to Methanol

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Global emissions of Carbon Dioxide (CO_2), a well-known greenhouse gas, have increased over the last centuries as it is one of the main products of fossil fuels combustion, the world's primary energy resource. Global warming is one of the major problems caused by this increase, thus it is essential to develop processes capable of converting CO_2 into valuable products [1]. The hydrogenation of CO_2 into methanol is an appealing research area since methanol is an alternative to fossil fuels, and it may enable the decline of CO_2 emissions and eliminate the release of harmful products, such as NO_x or SO_2 [1,2]. This reaction has thermodynamic limitations, as it is favored at high pressures and low temperatures. CO_2 activation is promoted at relatively high temperatures, nevertheless the selectivity for methanol decreases, with an increase in carbon monoxide (CO) production, as the *reverse water-gas shift* secondary reaction becomes predominant [3,4].

This study aims to assess the catalytic performance of Copper (Cu) and Zinc (Zn) bimetallic catalysts supported on pristine Activated Carbon (AC) and Carbon Nanotubes (CNT), and on composites with different proportions of CNT and Aluminum Oxide (Al_2O_3). The catalysts were prepared by incipient wetness impregnation and the composites by a ball milling treatment. The catalytic experiments to evaluate CO_2 conversion were conducted at 250 °C and 30 bar (*GHSV* = 24 000 cm^3/g h) with a Microactivity Reference reactor from PID Eng & Tech. The resulting gaseous products were analyzed with a Micro GC from Inficon. The catalysts and supports were characterized by different techniques, such as N_2 Physisorption at −196 °C, Thermogravimetric Analysis, Inductively coupled plasma - optical emission spectrometry, and Transmission electron microscopy analysis.

Preliminary catalytic experiments demonstrated that the catalyst supported on pristine CNT, CuZn/CNT, achieves slightly better catalytic results (higher CO_2 conversion) than the catalyst supported on pristine AC, CuZn/AC, leading to the preparation of catalysts supported on CNT:Al_2O_3 composites. It was observed an overall improvement in both activity and selectivity, confirming the possible benefits of combining the properties of carbon materials and metal oxide on composites, turning this approach an interesting toolbox for developing highly efficient catalysts for this reaction.

Acknowledgements

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Use of Oxidised Activated Carbon as Metal-Free Catalyst to Obtain Substituted Anilines

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Anilines are crucial industrial compounds used as intermediates in producing high-value chemicals, such as pharmaceuticals and polymers [1]. They can be synthesised by catalytic reduction of nitroarenes, the most economical and environmentally sustainable method, offering high atomic efficiency and selectivity [1]. Carbon-based materials have emerged as promising metal-free catalysts for this reaction due to their low cost, low toxicity, and easily adjustable properties through heteroatom doping [2]. In this work, a low ash-activated carbon (RGC30) has been modified for the catalytic reduction of 1-chloro-4-nitrobenzene. Two routes have been used; the first one consisted of oxidising the carbon with H_2O_2 to increase the acidic oxygenated groups (ROX) content. The second method involved subjecting the initial carbon to a heat treatment in O_2 (5 %v/v in He) at 420 ºC to obtain a carbon with surface groups of mainly basic character (RO2_10H). XPS studies showed an increase in the O content of the carbons, from ~2 at.% of RGC30 to ~8 at.% and ~10 at.% in ROX and RO2_10H, respectively. Furthermore, in conjunction with TPD (**Fig.1.a, b**), it was observed that the RO2_10H carbon had no carboxylic acid groups; however, the presence of lactones and anhydrides along with basic groups such as quinones could be observed. On the other hand, the ROX carbon showed a wide range of functional groups, from carboxylic acids to quinones. In addition, the carbons' textural properties were similar regardless of the oxidation method used. The catalytic test for the hydrogenation of 1-chloro-4-nitrobenzene shows that regardless of the oxidation treatment used, 100% selectivity was obtained for chloro-aniline. However, the oxidation method affects the catalytic activity (**Fig.1.c**). The ROX catalyst showed the highest conversion after 7 h of reaction despite having less total oxygen content. On the other hand, the ROX catalyst was thermally treated at 300, 500, 650 and 900 ºC to better analyse the effect of the oxygenated groups. It could be observed that all group types provide some catalytic activity. However, the carbonyl and quinone groups greatly influenced the activity.

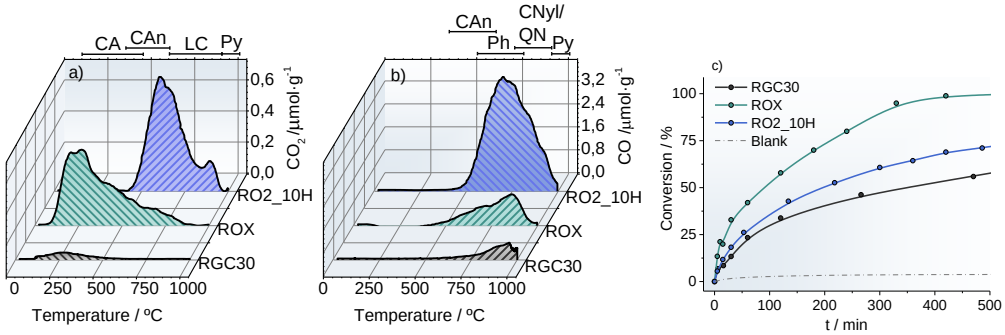

Fig.1. TPD for carbons before and after oxidation treatment: CO_2 (44 *m/Z*), **b)** CO (28 *m/Z*). **c)** catalytic oxidation of 1-chloro-4-nitrobenzene for coals before and after oxidation treatment.

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Palladium and Platinum hydrides as catalysts for enyne cyclosiomerization reaction and advanced solid state nmr spectroscopy

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In the fine-chemical industry, catalyst systems are used that consist of multiple components that must be combined in a specific way to generate the active catalyst species. Such association of the pre-catalyst species is therefore necessary to make the active catalyst, as is demonstrated in the seemingly simple example of the Pd-Zipper reaction [1]. However, if the association of the pre-catalyst species is disfavored, reaction rates will be low, and selectivity problems may arise.
In this study, we investigated the use of Pd(PCy3)2 in combination with chiral alcohols such as BINOL and its derivative phosphoric acid as pre-catalyst components. We measured the equilibrium constants of the oxidative addition to produce the active Pd-H species for various BINOL derivatives using solution NMR measurements. These catalyst systems are capable of enantioselective cyclization of substrate 1 which are measured as a function of sterics, acidity, solvent, concentration, and temperatures. The catalytic activity of these systems increases with increasing acid/alcohol concentration [2]. Additionally, COOH functionalized SBA-15 (varying pore sizes) are synthesized and tested as heterogenous acid. The equilibrium constants and the catalytic activity are compared to the homogenous system. Furthermore, surface immobilized Platinum hydrides[3] on metal oxides are investigated using 195Pt NMR spectroscopy [4].

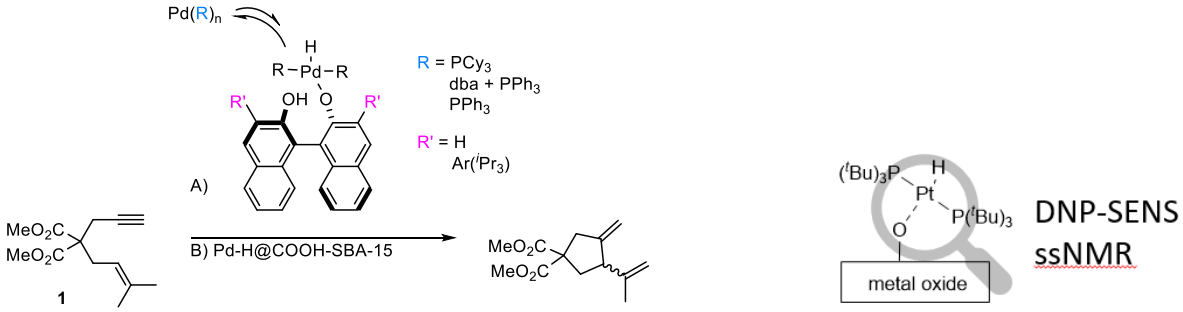

Figure 1: Scheme of Precatalyst equilibrium for enyne cycloisomerization homogenous (A) and heterogenous (B) (left) and surface Pt-H invesitgations.

The catalytic activity could be manipulated by varying concentrations. Additionally, surface reaction could inrease selectivity and stability. ^{195}Pt DNP-SENS MAS NMR showed promising results to characterize even low loading Pt containing catalysts. Structural motifs could be identified.

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Catalytic Hydrogenation for PFAS Removal

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Per- and polyfluoroalkylsubstances (PFASs) are among the most critical contaminants of emerging concerns (CECs) [1]. These anthropogenic compounds typically comprise a hydrophobic perfluorinated carbon chain alongside a hydrophilic functional group such as carboxylates sulfonates. This amphiphilic character provides them interesting surface properties, being used as cleaning products and emulsifiers [2]. PFAS were yet detected in human blood, plasma and urine [3]. Generally, PFASs do not degrade through normal chemical, physical, or biological processes.

Since 2016, there has been an increasing concern in monitoring PFASs in drinking water. Currently, the European Union Drinking Water Directive proposes a maximum limit of 500 ng/L [4] and 100 ng/L [5] for total and specific PFASs, respectively. Therefore, the development of treatment technologies for the removal and/or degradation of these pollutants is of the utmost importance. The motivation of this study is the development of catalysts combined with hydrogenation aiming at the degradation of perfluoroheptanoic acid (PFHpA), which belongs to the PFASs family.

Supported metal catalysts were synthesised using incipient wetness impregnation, with palladium and nickel serving as metals, and supported in carbon nanotubes and activated carbon. ZIF-67 catalyst was also synthesised using a co-precipitation method. All synthesised catalysts were texturally characterised before the reaction. The hydrogenation catalytic reactions were performed in a semi-batch reactor at ambient temperature and pressure, where 400 mL of a 150 µM solution of PFHpA together with 200 mg of synthesised catalysts were fed into the reactor, and a hydrogen flowrate (100 cm^3 min^{-1}) and stirring (800 rpm) were applied. To access PFHpA concentration, high-performance liquid chromatography (HPLC) analysis was performed.

Promising results were obtained from the experimental tests on the degradation of PFHpA. While complete degradation was not achieved, significant progress was made in breaking down these persistent compounds. The observed partial degradation indicates potential pathways and methods that could be further optimized and developed for more effective PFASs remediation. These findings underscore the potential of catalytic hydrogenation to contribute to the ongoing efforts to mitigate PFASs contamination.

Acknowledgements

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Development of 3D printed carbon-based macrostructures through direct ink writing

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Carbon materials have excellent properties for various applications, especially in environmental catalysis [1]. Most of the published studies report these materials in powder form, making them unattractive to be implemented in industrial processes since they pose challenges like handling difficulties, health risks, and the need for physical separation after reactions. Efforts to develop carbon-based macrostructures (CBMs) aim to address these issues, enhancing ease use in industrial processes. Challenges include structure stability, mechanical strength and mass transfer limitations (*e.g.* catalytic applications). Literature shows promising results with carbon material immobilization on inert supports like cordierite monoliths and membranes [2]. Additive manufacturing (3D printing) is a recent method that allows customized structure design, improving adaptability and performance in different reaction systems [3].

In this study, activated carbon (AC) and multiwalled carbon nanotubes (MWCNT) were used to develop CBMs. These materials are known for their effectiveness in environmental pollutant remediation. The CBMs were produced using direct ink writing (DIW), a 3D printing technique employing highly viscous, pseudoplastic inks. Sodium carboxymethylcellulose (CMC) and sodium alginate (ALG) were tested as binders and thickeners. The carbon materials were mixed with each binder, and then wetted with deionized water to create viscous inks. CBMs with carbon-to-binder ratios of 5:1 and 1:1 were developed and characterized by rheologic analyses, nitrogen physisorption at -196 °C, and scanning electron microscopy (SEM) to assess the pseudoplastic behaviour, textural properties, and microstructure of the 3D printed CBMs.

The inks were successfully used to print CBMs, confirmed by rheologic analysis showing pseudoplastic behaviour. Textural property analysis indicated possible blockage of inner cavities and pores in MWCNT and AC, particularly at a 1:1 mass ratio, confirmed by SEM micrographs showing film-like structures. These structures formed due to the water-soluble binders creating gels. The CBMs with a 5:1 mass ratio retained similar textural properties to raw carbon materials, suggesting they are the most promising, though future water treatment applications need validation.

Funding and acknowledgements

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Self-Supporting Films and Powders of Ordered Mesoporous Carbon based on Tailored Polyether Templates for Application in Electrocatalysis under Confinement

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"Reverse Pluronic" block copolyethers (PPOn/2-PEOm-PPOn/2) with tailored PPO block lengths (m = 90-450, n/2 = 20-200) were prepared using advanced, borane-based polymerization catalysis [1-4]. The thus obtained amphiphilic block copolyethers were then employed as nanostructure-directing agents in a soft-templating approach.

The mesoporous structure is generated by organizing the block copolyethers in EtOH together with oligomerized phenolic resins (= carbon precursors) in an evaporation-induced self-assembly (EISA) process [5-6]. Subsequent crosslinking (80-100 ºC) and carbonization (600-700 ºC) yields a series of mesoporous carbon materials (OMCs) with identical pore arrangement (hexagonal) and comparable surface properties – meaning the OMC samples differ only in their respective mesopore diameters (6-18 nm, depending on m and n/2) and are thus suitable for the identification of confinement effects [7].

In current work, these achievements are transferred to the preparation of self-supporting OMC films (100 µm thickness, 1-10 cm2). Essential parameters are pore arrangement (preferred: 3D-connected pore systems for better diffusion properties of the film), pore size, mechanical stability of the film and the presence of surface functionalities for subsequent catalyst immobilization.
OMC films carrying covalently bound Fe- and Co-porphyrin catalysts are used as thin film electrodes or gas diffusion electrodes for the electrocatalytic reduction of CO2, with the aim of producing C2+ products.

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Toward High-rate Carbon-based Supercapacitors: New Insights into Tuning Multimodal Mesoporosity in Hierarchical Porous Carbons

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Conventional porous carbon materials, such as activated carbons and carbon blacks, are attractive supercapacitor electrode materials due to their low cost of production and ultrahigh specific surface areas. However, their small electrolyte-accessible surface areas and slow ion transport in their micropores at high charging/discharging rates result in low specific capacitances, thereby limiting their energy densities [1]. Recent research has shown that hierarchical porous carbons (HPCs) offer the ultimate solution by combining the high surface area of micropores with the improved mass transport of ions in mesopores and macropores, thus rendering HPCs as promising high-rate supercapacitors [2].

Herein, we report the synthesis of monomodal and bimodal mesoporous HPCs utilizing a facile ice-templating method coupled with hard-templating using LUDOX® colloidal silica particles. In a typical synthesis, an aqueous mixture of glucose and colloidal silica particles is flash-frozen in liquid nitrogen. The ice fronts formed in the flash freezing process act as a soft template for macropores that can be removed by lyophilization, thereby yielding the dry glucose-silica matrix. The latter is then pyrolyzed, and the resulting carbon-silica matrix is stirred in an alkaline medium under reflux to etch out the hard template (colloidal silica particles). Nitrogen porosimetry was used to analyze the porous structures of the as-synthesized samples. The effect on pyrolysis temperature on the specific surface areas of the HPCs with monomodal mesoporosity was investigated, and the optimum temperature was used for the synthesis of the samples with bimodal mesoporosity. The roles of surface modifiers and size contrast of the silica particles in tuning the bimodal mesoporosity were also investigated.

Funding

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Degradation of pollutants in industrial effluents using ozonation reaction over Fe-catalysts

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Porous materials such as clay and activated carbon offer several possibilities for preparing heterogeneous catalysts due to their stability in different pH ranges, easy separation, and reutilization. Several examples can be found in the literature where clays [1] and activated carbon [2] are used as heterogeneous catalysts to eliminate pollutants from effluents. In this work, two different materials, a natural clay and a commercial activated carbon, were used as heterogeneous catalysts for the ozonation of real organic pollutants from a textile company (Fig1).
The raw clay was collected from the Middle Atlas region of Morocco ($Clay_{MA}$), which has huge deposits of clay minerals. This sample was ground, sieved to obtain particle sizes under 60 μm and used in this study without any prior activation. To compare the effect of the presence of the metal in the clay, activated carbon (Fe-ACp) catalysts were prepared by adding the same amount of iron (5.4 wt%) found in raw clay using an adapted method described in [3]. The best results were obtained with $Clay_{MA}$ on which 100% and 86% of conversion and mineralization, respectively, of the organic real effluent after 180 min of reaction.

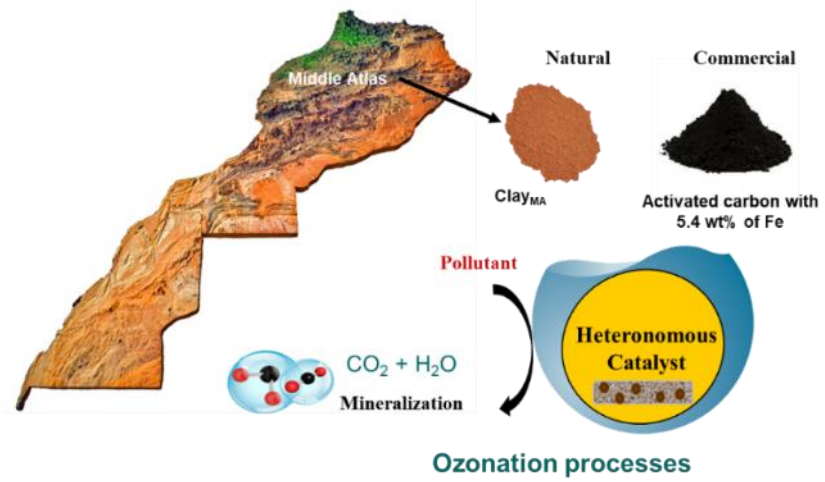

Fig 1. *Clay from Morocco and activated carbon as catalysts for ozonation oxidation of real pollutants*

Acknowledgements

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Proton-Electron Transfer From Well-Defined Molecular Hydrogen Donors To Metal Oxides

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Proton Electron Transfers (PETs) are referred as reactions of a proton H+ and electron e- from a hydrogen source to a reducible material such as metal oxides. These transfer reactions can occur in many processes rapidly in a single step or separately in multi-step reaction.[1] Well-defined molecular transition metal hydrides allow to tune the thermodynamic properties of the hydrogen source and provide important insights in to the reduction.[2] These hydrogen sources enable a selective reduction of catalytically active metal oxides such as MoO3[3], CeO2[4], V2O5 and Bi2O3, which are applied in a variety of different industrial processes. With our method we were able to show that, in addition to the surface area of the metal oxide, the morphology also makes an important contribution to the reducibility. Our work shows that the reduction of CeO2 with CpCr(CO)3H as a hydrogen source leads to a selective reduction of the surface by forming new surface OH groups, whereas the reduction of CpCr(CO)3H with V2O5 also leads to a bulk reduction by forming HxV2O5-X bronzes. We previously showed that HV(CO)4dppe reacts with MoO3 to result in a similar formation of hydrogen molybdenum bronzes. However, it is known that proton diffusion into the bulk of laminar materials, such as MoO3 and V2O5, is often anisotropic.[5] This means that diffusion between the layers of these materials is very fast while diffusion perpendicular to the layers is slow. In the case of V2O5, the 001 surface is perpendicular to the vanadium oxide layers and hinders diffusion of hydrogen atoms into the bulk while the 010 surface exposes the space between the layers. Furthermore, kinetic investigations show the kinetics vary significantly between different vanadium oxide samples (commercial > colloidal > nanowires > nanosheets) with different specific surface areas. The use of molecular transition metal hydrides as a hydrogen source provides a simple yet elegant method to model PETs at reducible surfaces to gain a deeper understanding of the surface chemistry of a material.

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11th Meeting of ENMIX Young Researchers

PROGRAMME

08:30 – 08:50	**Registration**
08:50 – 09:00	**Welcoming**
09:00 – 09:15	***Rafael Dias*** *Gas-Phase Simulated Moving Bed for Methane and Nitrogen Separation Using Maxsorb Extrudates*
09:15 – 09:30	**Klara Klemenčič** *Novel microporous zinc-based MOF for selective CO_2 capture*
09:30 – 09:45	**Harol Martínez** *Amino Acid Functionalized MOF-808 for CO_2 Capture: Unraveling the Host-Guest Interaction via INS Spectroscopy and DFT Calculations*
09:45 – 10:00	**Eric Fuster-Navarro** *Bactericidal Coatings of Photoactive Octahedral Molybdenum Clusters Embedded in a Polyurethane/acrylate Resin*
10:00 – 10:15	**Edgar Stiven Duran Uribe** *Nitroarene Hydrogenation Using Nitrogen and Phosphorus Co-doped Activated Carbon*
10:15 – 10:30	**Coffee Break**
10:30 – 10:45	**Wouter Van Hoey** *The bimetallic synergy of Pt with transition metals for the combustion of volatile organic compounds*
10:45 – 11:00	**Seda Yilmaz** *Electrocatalysis Under Confinement: CO_2-Reduction with Molecular Catalysts Immobilized on Ordered Mesoporous Carbons*
11:00 – 11:15	**Samar Al Jitan** *Photocatalytic conversion of CO_2 to methanol using copper oxide and vanadium oxide co-deposited on titania nanotubes*
11:15 – 11:30	**Coset Abreu-Jaureguí** *Surface Chemistry and Photodegradation: Insights into Heteroatom-Mediated Catalysis*
11:30 – 11:45	**Amrita Panigrahi** *Phosphine based Metal Organic Frameworks*
11:45 – 14:00	**Lunch Break**

14:00 – 14:15	**Mariana B. S. Felgueiras** *Hydrogenation Of CO_2 To Hydrocarbons With Multimetallic Carbon Catalysts*
14:15 – 14:30	**Mitra De Geest** *Chromium-containing Wastewater Treatment Using Clay-based Structured Composites*
14:30 – 14:45	**Sofia Santos** *Boosting catalytic potential and sustainability of carbon-coated macrostructured catalysts*
14:45 – 14:55	**Short Break**
14:55 – 15:10	**Assila Ouissal** *Catalytic Ozonation of Real Pollutants Using Raw Clay and Fe-Carbon Catalysts*
15:10 – 15:25	**Angela Severino** *Innovative System To Be Integrated Into Waste Water TreatmentPlants (WWTPs) For The Separation and Photodegradation OfMicro/Nano-plastics From Seawater*
15:25 – 15:40	**Izabela Majewska** *Catching the sunlight: CO_2 photoreduction on Cu-based polymeric carbon nitride and titania composites*
15:40 – 16:00	**Coffee Break**
16:00 – 16:15	**José Barbosa** *The feasibility of 3D-printed carbon-based macrostructures for oxalic acid ozonation*
16:15 – 16:30	**Valeria Vermile** *Evaluating The Impact Of Different Metal Oxides On Plasma Catalytic Dry Reforming Of Methane*
16:30 – 16:45	**Tatiana Zanette** *Ni-Zn paddle-wheel MOFs applied as catalytic precursors in ethylene dimerization reactions*
16:45 – 16:55	**Short Break**
16:55 – 17:10	**Meriem Abid** *Empowering the gas desulfurization efficiency of carbonmaterials through incorporating active inorganic phases*
17:10 – 17:25	**Ana Rita Querido** *Enhancing CO_2 Hydrogenation to Methanol with Carbon:Metal Oxides Composites as Catalysts Supports*
17:25 – 17:40	**Catarina Lopes** *Towards a sustainable world: catalytic degradation of 4- fluorophenol*
17:40 –	**Closing Ceremony and Social Event**

9th European Nanoporous Materials Institute of Excellence Workshop

BOOK OF ABSTRACTS

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