ZeoBioChem-SMS Academic Industrial Workshop (Hybrid)

20-21 October 2024, The University of Manchester

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Surface Measurement Systems
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Chair
Xiaolei Fan, The University of Manchester

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Location, venue and contacts:

The University of Manchester, Manchester, 20-21 October 2024

Workshop venue:

- James Chadwick Building_3.008, The University of Manchester, Booth St E, Manchester M13 9XH

Local contacts:

- Xiaolei Fan (xiaolei.fan@manchester.ac.uk)
- Shaojun Xu (shaojun.xu@manchester.ac.uk)

Travel information:

- **By Train:** **From Manchester Piccadilly (the main rail station), please see the map below for walking navigation.**
- **By Air:** **From Manchester Airport, you can either take a taxi or a train (to Manchester Piccadilly station) to the workshop venue.**
- **By Car:** **If you drive, you can use the Car Park Aquatics Centre (just opposite to the James Chadwick Building, the conference venue). Navigation: Booth St E, Manchester M13 9SS.**
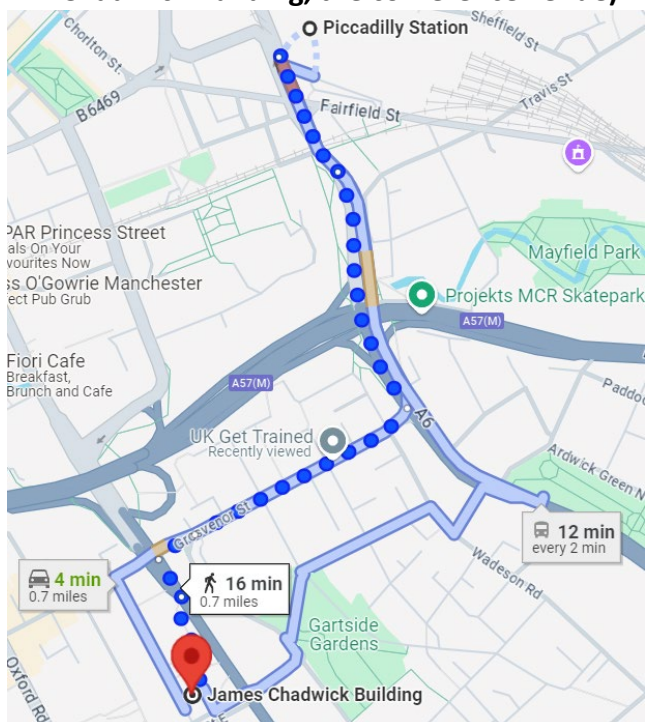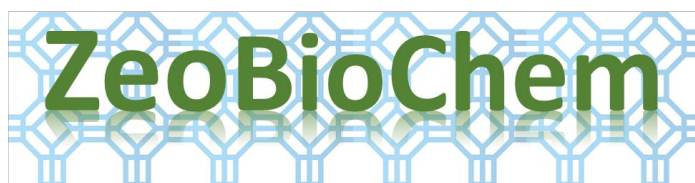

Workshop programme:

UK time (Sunday 20 October 2024)		
17:00	Social reception	**Brewdog DogHouse Manchester Bar & Rooftop** (18-20 Fountain St, Manchester M2 2AR)
18:30	Dinner	**Miller & Carter Manchester Steakhouse Restaurant** (53 King St, Manchester M2 4LQ)

UK time (Monday 21 October 2024)			
09:30	Opening	Xiaolei Fan, The University of Manchester	
Session 1: Chair: Xiaolei Fan, The University of Manchester			
09:40	Talk 1	Zhendong Liu, **Tsinghua University** (CST, UTC+8: 16:40)	Ultrafast Method to Encapsulate Metal Nanoclusters into Zeolites (**online**)
10:00	Talk 2	Risheng Bai, **Jilin University** (CST, UTC+8: 17:00)	Zeolite-Confined Pd Catalysts for Alkyne Semi-Hydrogenation (**online**)
10:20	Talk 3	Xin Gao, **Tianjin University** (CST, UTC+8: 17:20)	The microwave-assisted biomass pretreatment for component separation and process evaluation (**online**)
10:40	Talk 4	Norbert Miskolczi, **University of Pannonia** (CST, UTC+8: 17:40)	Zeolite catalyst application for bio-oil production and upgrading (**online**)
11:00	Talk 5	Chularat Wattanakit, **Vidyasirimedhi Institute of Science and Technology** (THA, UTC+7: 17:00)	Hierarchical zeolites for bioethanol upgrading: From laboratory-scale to pilot-scale (**online**)
11:20	**Tea break**		
Session 2: Chair: Chunfei Wu, Queen's University Belfast			
11:50	Talk 6	Xin Tu, **University of Liverpool**	Plasma Catalysis for Sustainable Production of Fuels and Chemicals
12:10	Talk 7	Lisa Mingzhe Sun, **Surface Measurement System**s	Realistic Evaluation of Prototypical Porous Materials for Carbon Capture
12:30	Talk 8	Muhammad Shahbaz, **Teesside University**	Intelligent System Integration for Optimal Deployment of Carbon Mitigation Solutions for NetZero Goal
12:50	Talk 9	Sean McIntyre, **Surface Measurement Systems**	Investigating polymeric membranes for CCS under industrial conditions
13:10	**Lunch**		
Session 3: Chair: Shaojun Xu, The University of Manchester			
14:00	Talk 10	Noemi Linares, **Universidad de Alicante** (CET, UTC+2: 15:00)	Superior Hierarchical Catalysts Prepared by Partial Interzeolite Transformation
14:20	Talk 11	Daniel Lee, **University of Manchester**	Contemporary methods to determine zeolite structures with solid-state NMR spectroscopy
14:40	Talk 12	Gabriela Duran-Jimenez, **University of Nottingham**	Single-step preparation of activated carbons from pine wood, olive stones and nutshells by KOH and microwaves: influence of ultra-microporous for high CO_2 capture (**online**)
15:00	Talk 13	Christopher Parlett, **University of Manchester**	Designing catalysts for cascade upgrading of biomass-derived substrates
15:20	**Group discussion**		
15:40	**End**		

Workshop organised as part of the European Union's Horizon 2020 research and innovation programme: Advanced Zeolite Catalysis for Sustainable Biorefinery to Produce Value-added Chemicals

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Ultrafast Method to Encapsulate Metal Nanoclusters into Zeolites

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The encapsulation of metal nanoclusters into zeolites has drawn considerable research interests, because this combination has opened up a new avenue to design zeolite-based bifunctional catalysts that offer high activity, shape selectivity and remarkable stability.[1] The driving force for the encapsulation is mainly van der Waals interactions, that is, the physical confinement of nanoclusters from zeolite frameworks. The encapsulation of metal nanoclusters into zeolites, however, is not an easy task. The main challenge comes from the fact that the formation of metal nanoclusters and the crystallization of zeolites are not on the same time scale.[2] In this work, we present a generalized, ultrafast method to encapsulate metal clusters into zeolites.[3,4] The success of this generalized approach lies in fastening the zeolite crystallization to match up with the rapid formation of nanoclusters. On this basis, we have successfully prepared a series metal-nanoclusters-encapsulating zeolites, such as PtSn@ZSM-5, PtZn@silicalite-1, PtNi@SSZ-13, CuO@silicalite-1, CoO@ZSM-5, in just a few minutes. The resultant metal-nanoclusters-encapsulating zeolites much outperformed those prepared by the conventional impregnation method. We further verified the successful encapsulation through applications such as ultradeep removal of H_2S and dehydrogenation of propane.

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Zeolite-Confined Pd Catalysts for Alkyne Semi-Hydrogenation

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The selective hydrogenation of alkynes to alkenes is a critical step in the synthesis of fine chemicals, with substantial applications across multiple domains, including pharmaceuticals, agriculture, and materials science. However, traditional palladium (Pd)-based catalysts are subject to inherent limitations in both activity and selectivity, often requiring a compromise in catalytic efficiency to achieve enhanced alkene selectivity.

Zeolites possess a wealth of pore structures, tunable compositions, and high surface areas, which effectively confine the active sites of noble metals. This study utilizes zeolites and amorphous zeolites as supports to immobilize Pd carbides or single-atom Pd, thereby significantly enhancing the activity and selectivity of Pd catalysts in the semi-hydrogenation of alkynes. Specifically, in situ carbonization reduction technology encapsulates sub-nanometer Pd carbide clusters within MFI-type zeolites. The resulting catalyst demonstrates exceptional performance under mild conditions in the semi-hydrogenation of alkynes, achieving a selectivity of 99% for the conversion of ethyne to styrene. The carbon species alter the electronic and spatial configuration of the Pd clusters by constructing Pd-C_4 structures and forming C-O-Si bonds with the Si atoms of the MFI zeolite framework, thus enhancing the catalyst's desorption capability for alkenes, leading to an increased selectivity for alkenes. Furthermore, by anchoring single-atom Pd on amorphous zeolites containing heteroatoms (e.g., B, Al, or Ga), a novel, highly efficient, and selective hydrogenation catalyst has been developed. The introduction of heteroatoms not only modifies the stereoelectronic configuration and electronic environment of the Pd active sites but also weakens the interaction between styrene and the catalyst, thereby enhancing catalytic activity and selectivity (95% for styrene selectivity and a turnover frequency of up to 24198 h^{-1}). Detailed structural characterization and theoretical calculations have elucidated the roles of carbon species and boron atoms in optimizing the electronic and geometric properties of the catalyst, as well as their promotional effects on alkene desorption. These strategies not only improve the performance of Pd-based catalysts but also provide new directions for their further optimization.

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The microwave-assisted biomass pretreatment for component separation and process evaluation

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Biorefinery of lignocellulosic biomass to produce biofuels for replacing fossil resources is a major topic of energy conservation and carbon reduction. Biomass pretreatment as an energy-intensive step during biorefinery process, can be integrated with microwave to achieve process intensification. This study compared the pretreatment performance between microwave heating (MH) and conventional heating (CH) to separate three major components in biomass using deep eutectic solvents (DES). Under the same pretreatment condition, the MH-assisted pretreatment consistently delivered better performance for separating three major components in biomass . The kinetic study was done using shrinking core model to reveal the behavior of biomass dissolution for CH- and MH-assisted processes. DES diffusion was the rate-controlling step for the initial stage of biomass dissolution, but surface chemical reaction dominated the subsequent stage. The rate constants of these two stages for MH-assisted process were always greater than those of CH-assisted process benefitting from the microwave intensification. In order to illustrate the economic and environmental feasibility of MH-assisted biomass pretreatment, the techno-economic (TEA) and life cycle assessment (LCA) for entire biorefinery process based on microwave-assisted DES pretreatment were done. For producing equlivant 1 kg product, the MH-assisted process could reduce greenhouse gas emissions by 4.85%. Under the same annual processing capacity of biomass 8000 t, the specific TAC regarding one-ton product for MH- and CH-assisted processes were 3194.35 and 3400.37 \$/(y·t), respectively. Obviously,the MH-assisted pretreatment possessed certain environmental and economic advantages.
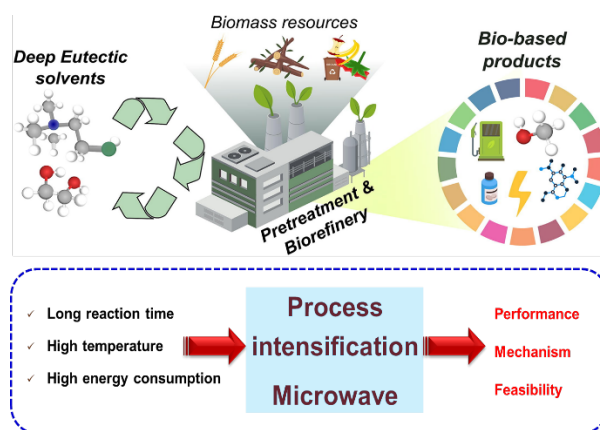

Fig.1 MH-assisted DES pretreatment to produce bio-based products.

Zeolite catalyst application for bio-oil production and upgrading

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Due to the significant increase in the amount of different wastes, the recycling of wastes has a great importance. Among the possibilities, different thermochemical methods play an important role. With these methods, waste can be transformed into valuable products. In the presence of catalysts, the product yields and composition can be further modified. Zeolites or their modified structures are mainly used as catalysts. Among others, bio-oil can be produced by the thermo-catalytic pyrolysis of waste, which must be further transformed before its further use. In this work, the catalytic pyrolysis of different wastes in a batch reactor was investigated at a temperature range of 300-600°C. Zeolites with different properties as catalysts were used. The characteristics of the products were investigated using chromatographic methods, FTIR method and standardized analytical methods. In order to improve the properties of bio-oil, hierarchical zeolite catalysts were synthetized, then the surface of which was modified with a transition metal. The catalyst obtained in this way was used to test the quality improvement of model bio-oil by esterification.

Hierarchical zeolites for bioethanol upgrading:

From laboratory-scale to pilot-scale

Chularat Wattanakit*, Peeranat Chaipornchalerm, Chadatip Rodaum, Anawat Thivasasith, Marisa Ketkaew, Ploychanok Iadrat, Peerapol Pornsetmetakul, Peeranat Chaipornchalerm, Watinee Nunthakitgoson, Supakorn Tantisriyanurak, and Anittha Prasertsab

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Bioethanol obtained from a renewable agricultural resource has become a promising feedstock for producing several chemical compounds, such as ethylene, diethyl ether, and acetic acid. In this contribution, we report the new approach for the catalyst design based on zeolites and zeolite composites with hierarchical structures[1-8]. Various hierarchical zeolite frameworks have been synthesized by a simple hydrothermal process, such as ZSM-5, MOR, and FER. The designer catalysts exhibit outstanding physicochemical properties in particular high surface area and porosity, and suitable acidity, eventually improving catalytic performances in bioethanol conversion to ethylene[2-6]. To gain insights into the mechanistic perspectives of bioethanol conversion, we also integrated *in-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) studies and density functional theory (DFT) calculations to understand the effect of different zeolite frameworks on the catalytic transformation of bioethanol.

To develop the industrial catalysts, the rational design of binder-free hierarchical ZSM-5 monolith derived from zeolite@layered double hydroxides (LDH) composites via traditional extrusion and 3D printing technologies has been demonstrated[3]. The designer catalyst applied in bioethanol dehydration boosts ethylene yield by over 96% due to the synergistic effect of zeolites and LDHs. This is the first example illustrating the design of highly efficient catalysts, which can be applied directly in industrial applications. Last but not least, we also illustrate the application of the designer catalysts in the bioethanol dehydration to ethylene on a pilot-plant scale. This example opens up new perspectives on the industrial catalyst design for bioethanol upgrading applications.

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Plasma Catalysis for Sustainable Production of Fuels and Chemicals

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The conversion of inert molecules (e.g., CH_4, CO_2 and N_2) with strong chemical bonds into value-added fuels and chemicals has attracted significant interest. However, the activation of these molecules remains a great challenge due to their thermodynamic stability, which requires a substantial amount of energy for activation. Non-thermal plasma (NTP) has emerged as a promising technology for gas conversion under mild conditions [1-3]. The combination of NTP with heterogeneous catalysis holds great potential for achieving a synergistic effect through interactions between the plasma and catalysts. These interactions can activate catalysts at low temperatures, improve their activity and stability, and lead to notable increases in conversion, selectivity, and yield of end-products, as well as enhance the energy efficiency of the process. Furthermore, plasma processes can be switched on and off instantly, offering great flexibility in decentralised fuel production using renewable energy sources, particularly intermittent renewable energy. This lecture will discuss the opportunities and challenges in plasma-catalytic gas conversion to fuels and chemicals, including various chemical processes such as NH_3 synthesis, CO_2 conversion and CH_4 activation.

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Realistic Evaluation of Prototypical Porous Materials for Carbon Capture

Lisa Mingzhe Sun[1], Sean McIntyre[1], Majid Naderi[1], Daryl Williams[1,2] [*]

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Carbon capture, utilization, and storage (CCUS) is an attractive approach to help decarbonization from point sources, like energy supply and other industries, as well as for pulling CO_2 out of the atmosphere (i.e., direct air capture, DAC). Among several approaches at differing technology readiness levels, solid sorbents are promising as they generally combine high uptakes and selectivity with milder regeneration energies.

Adsorption screening and testing of promising materials are often performed using pure component or point uptake experiments, which only give information about adsorption capacity and ideal selectivity. At realistic process conditions, competitors such as moisture and temperature have a large effect on the uptake of CO_2, wherein the presence of water could either increase CO_2 capacity, compete for the same adsorption sites, or even induce material collapse. The kinetics on the other hand is another important factor for an effective separation.
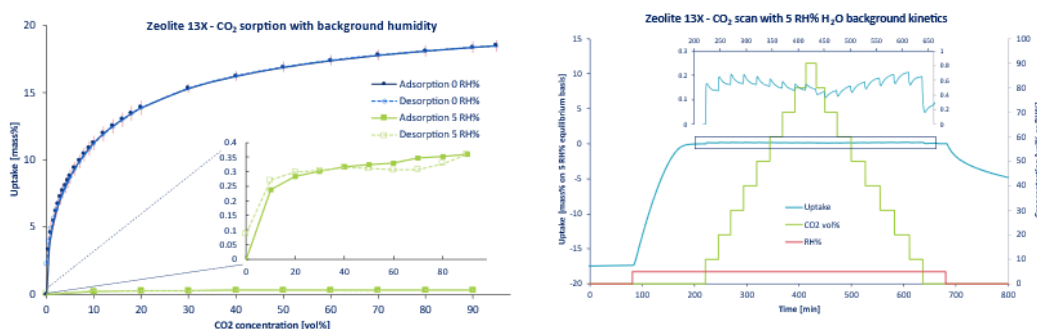

Figure 1. (a, left) Apparent CO_2 uptake decrease by 5% RH in Zeolite 13X and (b, right) detail of the sorption kinetics of both components highlighting replacement effects.

In this work, several porous materials including zeolites, MOFs, and functionalized resins are screened in realistic conditions for CO_2 capture using advanced dynamic gravimetric sorption and breakthrough methods. The tests were conducted under varied conditions, e.g., different CO_2 concentrations and relative humidity. The results showed that humidity is the key factor affecting CO_2 capture efficiency. This study provides a reference for screening the effective sorbents for carbon capture.

Intelligent System Integration for Optimal Deployment of Carbon Mitigation Solutions for NetZero Goal

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Abstract: This study aims to develop an intelligent system by integrating various CO_2 mitigation technologies. Three technologies are evaluated for their capacity to mitigate one ton of CO_2: Direct Air Capture (DAC), Bioenergy with Carbon Capture and Storage (BECCS), and Biochar production through pyrolysis. Process models are created for each method, followed by techno-economic analyses and optimization to identify the most effective solution. This comprehensive approach addresses objectives such as net energy gain, minimized water usage, and product sales. The results indicate that BECCS is the most promising in terms of net energy gain, delivering approximately 18.08 GJ, with Biochar closely following at 15.08 GJ. Biochar is also notable for its lower water consumption of 2.3 m³ compared to BECCS's 3.03 m³, while DAC demonstrates significantly higher water usage and energy demand, requiring 11.95 GJ. The economic analysis aligns with these findings, showing product sales of $756 million for Biochar, $233 million for BECCS, and $60 million for DAC. The optimization process identified 22 potential solutions based on the energy, water usage, and sales nexus. The most favorable solution combines 53% Biochar and 47% BECCS, considering factors such as net energy gain, water conservation, product costs, and the technologies' technical maturity.

References

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Investigating polymeric membranes for CCS under industrial conditions

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An attractive type of membrane material for CCS applications are polymers with intrinsic microporosity (PIMs) – forming flexible and easy-to-manufacture single-component membranes with high gas permeabilities and selectivity for CO_2 over N_2 and O_2 – primary components of flue gas. In this work, a novel membrane analyzer was developed to observe the multi-component permeation of flue gas constituents through membranes of PIM-1 and its more hydrophilic carboxylate functionalized version, cPIM-1, to reveal the impact of contaminants and industrial process conditions on the membrane separation efficiency.

Humidity was first introduced to the membranes for 3 hours, followed by 10% CO_2 in N_2 whilst maintaining the selected humidity. The permeation curves were measured using CO_2 and humidity probes at the inlet and outlet, with nitrogen measured using a TCD.

The carboxylated PIM-1, cPIM-1, was studied under the same conditions as PIM-1. The carboxylation is known to make the cPIM-1 membrane more hydrophilic and thus the effect of increasing relative humidity was found to be more pronounced, with a 40% decrease in CO_2 permeation observed in cPIM-1 compared to the 20% decrease observed for PIM-1. The CO_2/N_2 selectivity of cPIM-1 was found to decrease by 20% over the same humidity range.
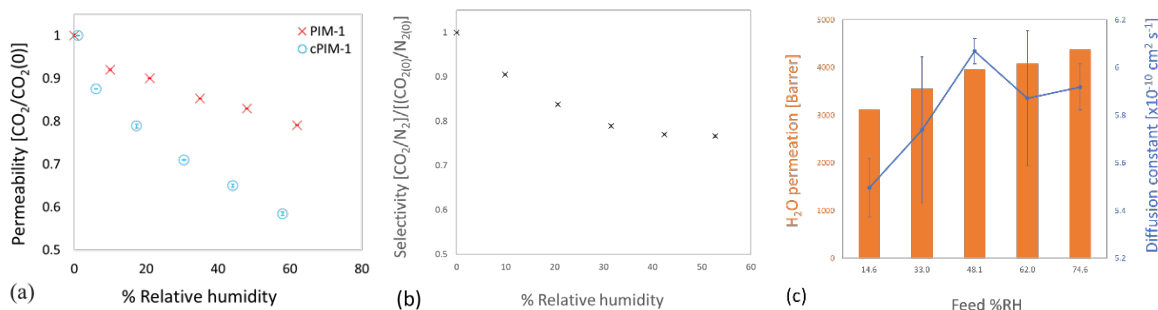

Figure 1: (a) The impact of humidity on PIM-1 and cPIM-1 CO_2. (b) cPIM-1 CO_2/N_2 gas selectivity change due to humidity (c) The impact of humidity on water permeation through cPIM-1

Further studies were undertaken using Dynamic Vapor Sorption (DVS) to confirm the membrane uptake behavior, most importantly that of water in the Langmuir voids [1,2] of the polymers and the subsequent impact of this water build-up on CO_2 uptake.

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Superior Hierarchical Catalysts Prepared by Partial Interzeolite Transformation

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A new family of X-ray amorphous zeolites with unique structural properties was prepared by partial interzeolite transformation. [1,2] We realized this strategy for two different interconversions (FAU to BEA and FAU to MFI) and various synthetic approaches. The resulting ITIs (Interzeolite Transformation Intermediates) are composed of zeolitic building units, and display both enhanced accessibility and strong acidity. This method allows to fine-tune the properties of the solids by simply interrupting the interconversion of different times (Fig. 1 A-D). We have evaluated the potential of these materials for the conversion of bulky molecules for a number of reactions including Friedel–Crafts alkylations, the Claisen–Schmidt condensations, and the cracking of bulky molecules (Fig. 1 E-G).
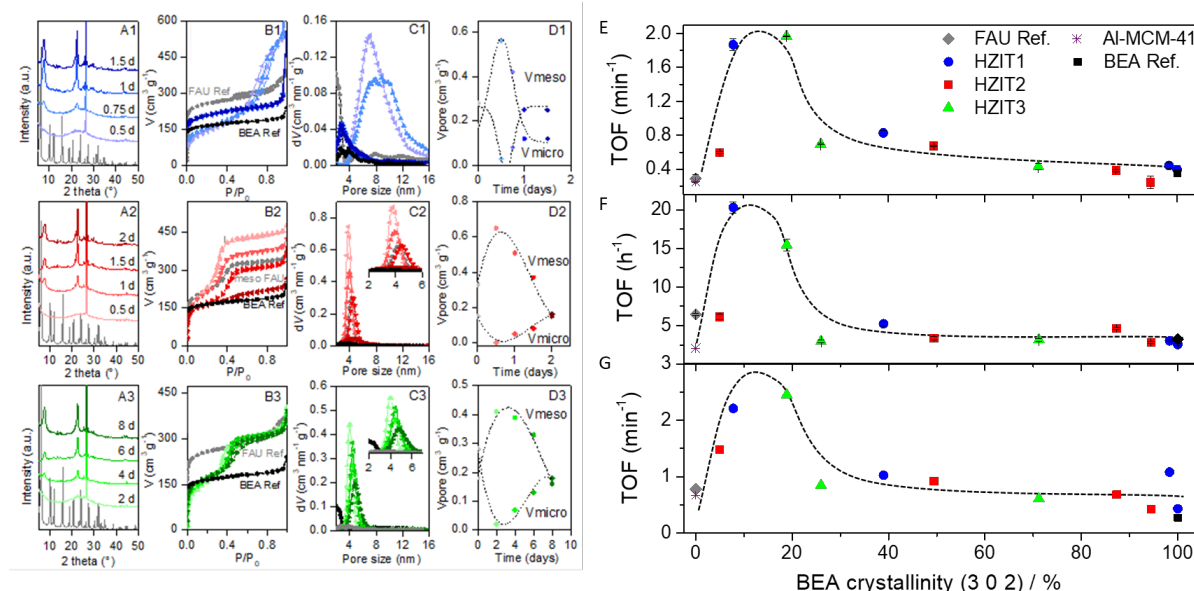

Figure 1. a) Structural and b-d) textural characterization of the ITIs from FAU to BEA zeolite. Catalytic performance of these materials for the e) Friedel–Crafts alkylation of indole with benzhydrol, (f) Claisen–Schmidt condensation of benzaldehyde and hydroxyacetophenone, and (g) polystyrene cracking.

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Contemporary methods to determine zeolite structures

with solid-state NMR spectroscopy

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Surfaces and interfaces play a major role in determining the characteristics of high surface area functional materials such as zeolites, whether they are providing active sites for heterogenous catalysis or for adsorption. Detailed rational control over the surface chemistry, thus enabling a fine tuning of these properties as well as substantial modifications, requires an in-depth understanding of the interfacial atomic environments.

Here, we will look at the role that contemporary methods for solid-state NMR spectroscopy can play in understanding the atomic-level structures of zeolite interfaces. These methods include the use of ultra-high magnetic fields (23.5 T), low temperatures (100 K), and probe molecules for NMR spectroscopy. This will provide information on the function of the active sites, synergistic effects between active sites, as well as mechanisms for catalyst degradation. This will be shown for various hierarchical zeolites as well as for a bimetallic aluminum- and niobium-doped porous framework that efficiently converts biomass-derived 2-methyltetrahydrofuran to pentadienes (see figure)[1]. This gives us a powerful tool to help rationalise chemical modifications to facilitate further improvements in these functional materials.
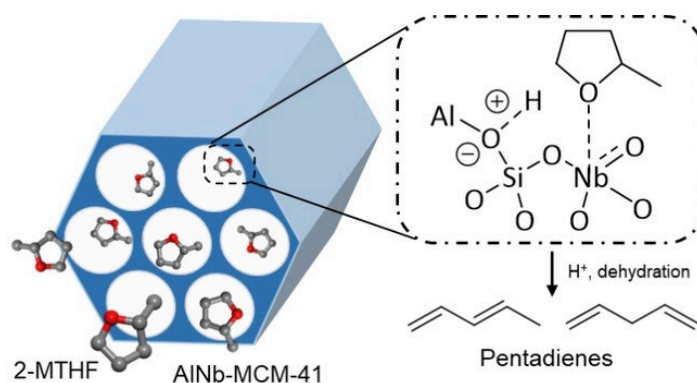
References

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Single-step preparation of activated carbons from pine wood, olive stones and nutshells by KOH and microwaves: influence of ultra-microporous for high CO2 capture

Gabriela Duran-Jimenez*[1], Jose Rodriguez[1], Lee Stevens[1], Sanad Altarawneh[1], Andrew Batchelor[1], Long Jiang[1], Chris Dodds[1]

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Abstract

Biomass residues are crucial feedstocks for facing climate change challenges due to high-value products, such as producing activated carbons (AC) for carbon capture. Two stages of pyrolysis followed by activation at high temperatures are the most used technique for converting lignocellulosic precursors into porous activated carbons. This process has shown to offer the highest surface areas; however, a two-stage process is undesirable as is an energy-intensive processes. Product characteristics are affected by feedstock and reaction rate conditions. In the present study pine wood (PW), olive stones (OS) and pecan nutshells (NS) were evaluated as feedstocks in the production of AC for selective post-combustion CO_2 capture via a single-step pyrolysis-activation using microwave heating. Direct raw biomass impregnation was completed using potassium hydroxide (KOH). The ACs were synthesised in 8 min using 300 W of microwave power with 8.8 GJ t^{-1} specific microwave energy input. Samples exhibited large specific surface areas (S_{BET}), up to 1340 m^2g^{-1}, with 70% of ultra-micropores (<0.8 nm), fundamental for high CO_2 adsorption capacity. Among the tested biomasses, PW was the best performing and physicochemical characterisation and CO_2 capture studies indicated that PW-based AC has 79% carbon, amorphous structure, and possessed larger ultra-micropores that resulted in high CO_2/N_2 selectivity (12.5), and one of the largest CO_2 uptakes for ACs (6.2 and 4.2 mmol g^{-1} at 0 and 25 °C, respectively). The CO_2 performance was investigated across a range of temperatures up to 100 °C, while cyclic regenerative performance was confirmed after 15 adsorption-desorption cycles. This study highlights the development of AC from different lignocellulosic resources by a fast and low-energy single microwave-pyrolysis activation process that can produce ultra-microporous structures implemented in post-combustion CO_2 capture[1].
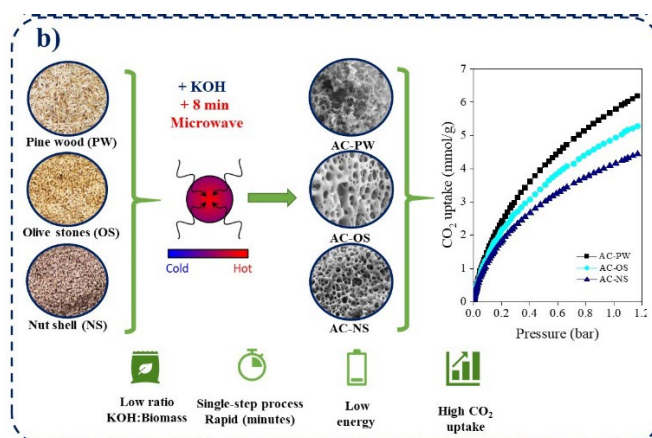
Fig. 1 Schematic representation of ACs produced in single-step with MW heating.

References

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Designing catalysts for cascade upgrading of biomass-derived substrates

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Cascade reactions are sequential chemical transformations in which the starting substrate undergoes a reaction whose product becomes the substrate for the next step, and so on, until a stable product is reached.[1] Cascades offer great advantages with respect to atom economy, and time, labour and resource efficiency management, whilst permitting the use of synthetically enabling intermediates that may be impractical to isolate. However, catalytic cascades, in which the product of a reaction catalysed by species A undergoes a subsequent distinct transformation catalysed by a second species B, are hindered by the possibility of undesired interactions between the initial substrate and the second active site, or indeed between the two catalytic species. Thus, highly desirable 'one-pot' catalytic cascades necessitate the spatial separation of each catalytic step. Here, we report generic routes to new classes of spatially orthogonal (i.e. mutually exclusive) bifunctional porous materials comprising hierarchal bimodal porous skeletons that enable the chemical environment of distinct pore regions to be independently tuned, which in turn regulates active site accessibility and communication between different spatially localised catalytic functionalities. Hierarchical porous architectures have been synthesised via either dual templating strategies or the desilication of commercial microporous zeolites. Controlled active site deposition, through either blocking of locations by pore templates or through size limitations, allows for the coupling of complementary sites, including two distinct metal nanoparticles (NP), an acid and a base, and an acid and metal NPs. These configurations are tuned for one-pot alcohol selective oxidation,[2] transesterification and esterification,[3] and hydrodeoxygenation cascades,[4] and demonstrate unique and optimal catalytic performances and properties when evaluated against conventionally prepared catalytic systems.

References

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