

IT1: Gold catalysts for cleaner industrial applications: Recent successes and future outlook

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Since its discovery as a catalyst, gold has been found to be not only active but the best candidate for a number of important reactions. This talk will give an overview on the discovery, optimisation and successful commercialisation of a supported gold catalyst for the hydrochlorination of acetylene, replacing the highly toxic mercuric chloride catalyst. In addition, promising new examples of the use of gold as a catalyst will be discussed, such as in the oxidation of methane to methanol, and how these can pave the way for future clean applications.

IT2: Shaping the future of catalysts

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Catalyst shaping technology is a topic which is often overlooked in catalyst research, mainly due to the size of the reactor required for accurate testing, compared to small bench-top reactors designed for powders. However, for a commercially viable catalyst, the shape of the catalyst must be considered and, in some cases, can be the main dictator of the overall performance of a catalyst in a commercial reactor. This presentation will give an overview into the importance of catalyst shaping and will also detail how BASF is using cutting edge computational techniques in combination with innovative manufacturing processes to access new shaping options for commercial catalysts.

IT3: Heterogeneous catalysis for a sustainable industry – an applied industrial perspective

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Catalysis is a key pillar of Green Chemistry and is hugely important for the manufacture of most chemical products, adding significant value to global GDP. Heterogeneous catalysis is the most used branch of catalysis but is still undervalued. Other forms of catalysis such as biocatalysis are currently ‘in vogue’.

The talk will consider heterogeneous catalysts and the use of PGM’s from a sustainability perspective, including some of the challenges to initial investigation and successful scaleup. The standard principles of sustainability; reduce, reuse, recycle, are imperative to the continued use of these precious resources. Two case studies will be used to highlight some of the challenges with the development of heterogeneous catalytic processes within Pharmaceutical environments.

IT4: From zeolite powder to industrial catalyst for sustainable industry: an overview of the scale-up and industrialization process

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Zeolites are natural or synthetic microporous crystalline oxides widely used in industry as catalysts or adsorbents. The past decade has witnessed a continuous expansion in the application of zeolites for various applications in the field of the production of petrochemicals (i.e. alkylation, isomerization) and fuel (i.e. FCC, hydrocracking) but also in the post-treatment of exhaust gas.

Synthetic zeolites are usually prepared by hydrothermal treatment of a reactive gel under autogenous pressure. The resulting product is a powder containing crystals with sizes in the micrometer range. To be used in an industrial process, these crystals will usually have to be modified but also will have to be shaped into a suitable form for any specific application.

This presentation will give few examples of how zeolites could be use as heterogeneous catalyst for sustainable industry and show the steps needed to move a zeolite from a lab scale synthesis to an industrial product.

IT5: A revisit to the longstanding dealumination and desilication of synthetic zeolites

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Synthetic zeolites, such as FAU Y and MFI ZSM-5 zeolites, are industrially important solid acid catalysts, especially in petrochemical fluid catalytic cracking (FCC) for producing gasoline range and gaseous (such as propylene) products. Reactivity, selectivity and accessibility are important features of bulk zeolites, being critical to determine the performance of industrial FCC catalysts. Specifically to address accessibility issues associated with the microporous zeolites (or diffusion limitation in the framework), various strategies are being developed and explored to enhance the rate of diffusion reactants/products into/from the zeolites, such as the design of nanozeolites, the templating method to prepare zeolites with mesoporous features and the post-synthesis modification methods to prepare hierarchical zeolites. Among these developments, the post-synthesis methods (such as dealumination and desilication) are robust and practical with low-cost implications, and used by the industrial, being deemed as unlikely to have breakthrough development. In this keynote presentation, by revisiting the mechanisms of dealumination of low Si/Al Y zeolite and the desilication of ZSM-5 zeolite, we propose new strategies to improve the old techniques further with relevant findings to show the developed hierarchical mesoporous FAU Y and mesoporous low Si/Al ratio hollow ZSM-5 zeolites, as well as their catalytic performance in model cracking reactions.

IT6: Exploiting novel supports in heterogenous catalysis

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Carbon nanostructures (CNS) have recently become of great interest for use as nanoreactors in a variety of different catalytic chemical reactions as they are robust, chemically inert, and available in a large range of well-defined pore shapes and sizes. Most importantly, due to recent advances in production, CNS are now readily available in large quantities at low cost which opens up the potential for application in large-scale preparative syntheses for the first time. This talk will outline how nanostructured carbon support materials have been developed in which the shape of the carbon at the nanoscale is tailored to influence both the stabilisation of the NPs and the efficiency of chemical reactions. So-called carbon nanoreactors can lead to enhanced reaction rates and changes in selectivity of reactions simply as a product of the dimensions of pores within the structures.¹ The shape of the pore can also be exploited to stabilize metal NP catalysts, reducing leaching and loss of activity.²

Adoption of high throughput, heterogenous catalysis at scale will enable robust, continuous manufacture. However, industrial application of carbon nanoreactor catalysts has been limited to date by the fact that they exclusively exist as powders which are difficult to pack in catalyst beds without being compressed into plugs which cause huge back pressures in flow systems. One potential solution to this problem, adopting the approach pioneered by HPLC column manufactures, is to utilize smaller, spherical, mono disperse catalyst pellets (50-700 μm) with a particle size distribution that is as narrow as possible (ideally $\sigma \ll 0.1$). In addition, the pellets need to be resistant to crushing within the bed, porous, to maximize the available reactive surface and able to support/stabilize metal nanoparticles catalysts in a way which prevents leaching over time.

Development of novel carbon based, pelleted catalyst materials, in which nanoparticles can be deposited controllably to give homogeneous, egg shell or egg yolk distributions by altering the deposition procedure has been undertaken. These innovative catalyst beads have been integrated into a lab scale trickle bed reactor enabling heterogenous catalysis to be performed using the self-optimizing, reactor platforms at the University of Leeds. This provides a route to optimisation of reaction conditions and scale up of heterogeneously catalysed chemical reactions in flow.³

¹ Aygün, M.; Stoppiello, C. T.; Lebedeva, M. A.; Smith, E. F.; Gimenez-Lopez, M. C.; Khlobystov, A. N.; Chamberlain, T. W. Comparison of alkene hydrogenation in carbon nanoreactors of different diameters: probing the effects of nanoscale confinement on ruthenium nanoparticle catalysis. *Journal of Materials Chemistry A*, 2017, 5, 21467-21477.

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³ Manson, J. A.; Clayton, A. D.; Labes, R.; Niño, C. G.; Chamberlain, T. W.; Blacker, A. J.; Kapur, N.; Bourne, R. A. A Hybridised Optimisation of an Automated Photochemical Continuous-Flow Reactor, *CHIMIA* 2019, just accepted.

T1: A chemo-enzymatic oxidation cascade to activate C–H bonds with in situ generated H₂O₂

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The use of chemo-catalysts combined with enzymes in cascade processes has emerged as a new potential chemical technology in recent years for facile chemical synthesis with improved atom efficiency. The use of such cascades is viewed as a way of combining the advantages of both types of catalysts to obtain high chemo-, regio- and stereo-selectivities, together with functional group tolerance and high reaction yields.

Selective oxidative C–H activation of hydrocarbon substrates remains a challenge for both heterogeneous catalysis and biotechnology. Peroxygenases have been described as “ideal catalysts” for CH-activation because they are relatively stable with high efficiency toward H₂O₂ and in addition do not, like P450 monooxygenases, require cofactors that need regeneration. Several systems have been developed to supply H₂O₂ to UPOs including additional enzymatic reactions, photocatalysis and electrocatalysis resulting in complex reactor setups. A simple alternative would be to directly generate H₂O₂ from H₂ and O₂ with supported gold-palladium (AuPd) heterogeneous catalysts which have been shown to be able to achieve H₂ selectivity of >95% towards H₂O₂. This would make an atom efficient process possible and could represent an approach that does not require any significant re-design of current catalytic reactors however the heterogeneous catalysts typically operate at reaction conditions much too harsh for enzymatic processes.

Our results show that in the presence of a range of highly active H₂O₂ generating catalysts, which can produce H₂O₂ at ambient temperature, pressure and in buffered aqueous solution the bio-catalysts activity is maintained towards unactivated C–H activation with high selectivity towards the primary hydroxylated product for a range of substrates (Figure 1). In addition, this tandem catalysis system can carry out the chiral transformations associated with the enzyme only system and maintain the highly enantiomeric excess (e.e. 98%+) of the hydroxylation reactions including ethylbenzene, propylbenzene and tetralin hydroxylation to alcohols at mild conditions with water only as the byproduct¹.

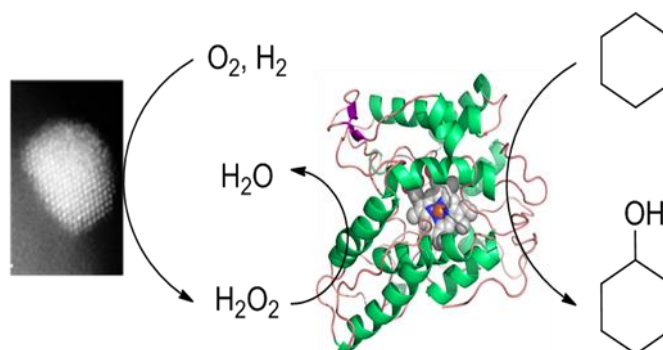


Figure 1 Schematic chemo-enzyme cascade with in situ H₂O₂ formation for cyclohexane oxidation

This approach shows that heterogeneous catalysts and biocatalysts can operate in the same reactor in a cascade manner – opening the possibility of reaction cascades using the benefits of both systems leading to more sustainable chemical processes.

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T2: Non-thermal plasma (NTP) activated heterogeneous catalysts for catalytic CO₂ hydrogenation

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Introduction

Non-thermal plasma (NTP) technology is a promising alternative to the conventional thermal system for activating heterogeneous catalysts at ambient conditions, presenting several advantages such as ease of handling, system compactness and process versatility¹. Specifically, plasma as a neutral ionised gas is categorised as the fourth state of matter, having energetic species such as highly excited molecules, atoms, ions, free radicals, electrons, and photons. Such energetic species have a great potential in activating heterogeneous catalysts and molecules, and thus intensifying the chemical reactions to produce desired products under mild conditions. Recently, many kinetic studies have been undertaken in order to understand the synergistic effects and mechanisms of plasma-catalyst interactions for methane activation and conversion. However, the effects of NTP-catalyst interactions for catalytic CO₂ hydrogenation are rarely evaluated kinetically in previous studies. The present study demonstrates that catalytic CO₂ hydrogenation can be performed under ambient condition employing NTP activated Ni/SiO₂ catalyst. We describe the results of a systematic evaluation of the kinetic effects of NTP driven catalytic CO₂ hydrogenation. Kinetic studies were systematically performed to understand the combined effect of NTP activated catalytic CO₂ hydrogenation system compared to the thermal system.

Materials and Methods

The 10Ni/SiO₂ catalyst was prepared by a conventional incipient wetness impregnation method. Specifically, SiO₂ was impregnated with the nickel nitrate aqueous solution for 12 h and dried at 80 °C. Then the resulting solids were calcined in a muffle furnace at 450 °C in air for 6 h with a ramp of 5 °C min⁻¹. The NTP-assisted CO₂ hydrogenation over Ni/SiO₂ catalyst was carried out in a continuous-flow dielectric barrier discharge (DBD) plasma reactor (Figure. 1) at atmospheric pressure without an external heat source. In a typical experiment, 100 mg of the as-synthesised catalyst was packed in the discharge area between ground electrode and quartz reactor body. The plasma was generated by an alternating current high voltage power supply with a peak voltage of up to 40 kV and a variable frequency of 20–70 kHz. Prior to reaction, the catalyst was pre-treated using plasma under 6.5 kV with pure H₂ as the discharge gas (flow rate = 50 mL (STP) min⁻¹) for reduction. In order to have a systematic kinetic understanding of the CO₂ methanation via Ni/SiO₂ catalyst activated by NTP, different applied voltages and H₂ partial pressures were studied. The data of the power of the plasma system was collected via a digital oscilloscope (TBS1102B) with a high voltage probe (P6015A).

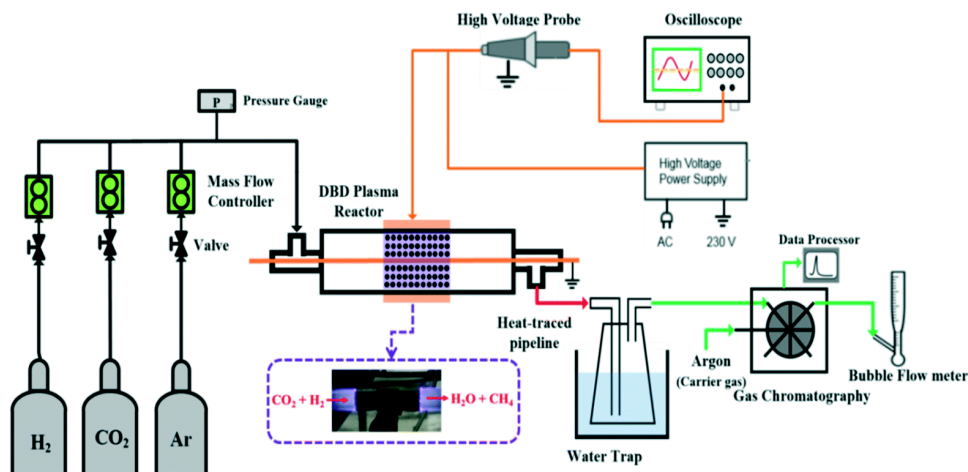


Fig 1. Schematic diagram of the experimental rig for NTP-assisted catalytic CO₂ methanation

Results and Discussion

Figure 2a shows that the thermal catalysis exhibits a typical Arrhenius behaviour which allows the calculation of EA, thermal as $\sim 70.25 \text{ kJ mol}^{-1}$, being comparable to the previous reported value (i.e. $\sim 68.9 \text{ kJ mol}^{-1}$). For the NTP-assisted system, as shown in Figure 2b, the linear fit of the plot of the reaction rate of NTP-activated catalysis ($\ln r_{\text{NTP-cat}}$) against inverse DBD discharge power ($1/\text{power}_{\text{DBD}}$) was performed, resulting EA, NTP = $\sim 31.95 \text{ kJ mol}^{-1}$, which is 55% lower than that by the conventional thermal catalysis. Furthermore, the reaction temperature of the NTP-activated catalysis was also recorded to plot the Arrhenius plot as shown in Figure. 3.

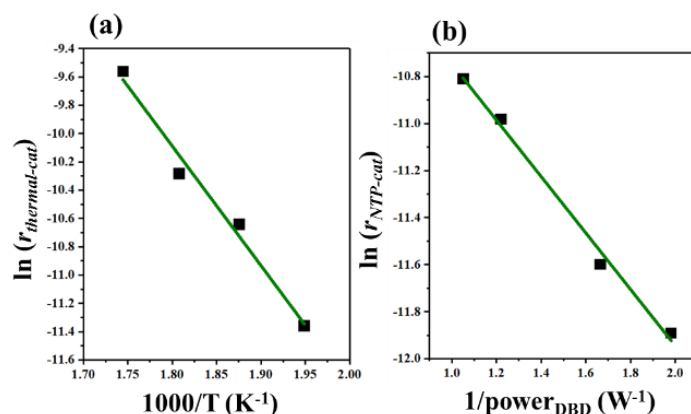


Figure 1: (a) Arrhenius plot of the thermally activated catalytic CO₂ hydrogenation over the 10Ni/SiO₂ catalyst, (b) the $\ln r_{\text{NTP-cat}}-1/\text{power}_{\text{DBD}}$ plot of the NTP-activated catalysis

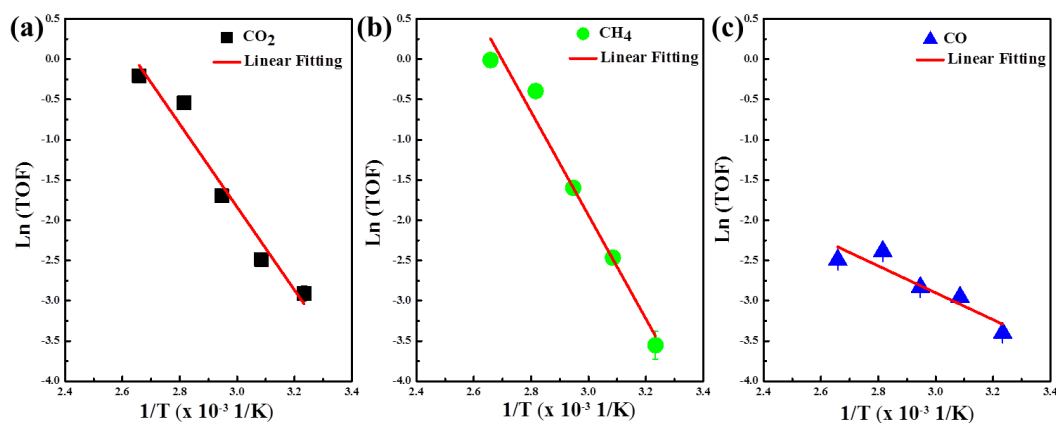


Figure 2: Arrhenius plot of the NTP-activated catalytic CO_2 hydrogenation over the 10Ni/SiO_2 catalyst

Significance

Our previous studies showed that the electronically excited gas species (e.g. CO_2 , H_2) and radicals generated in NTP catalytic system could readily interact with Ni catalyst surface, and thus the catalytic CO_2 hydrogenation process could be significantly intensified by NTP-promoted surface reactions. In this work, we have a systematic evaluation of the kinetic effects of NTP driven catalytic CO_2 hydrogenation including the effect of different input energy, H_2 partial pressure and feed flow rate to the kinetic. A better understanding of the plasma-catalyst interactions for methane activation and conversion.

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T3: New frontiers in catalysis: 3D printed reactors for sustainable chemistry

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Structuring the catalysts into multi-channel reactors and bespoke 3D printed architectures leads to greatly improved productivity/conversion due to the high surface area and precise and uniform product distribution in comparison to the conventional randomly packed beds of catalyst bodies.



The rising demand for 3D printing technology is due to the method's suitability as a means of controllable deposition of support and active material in order to produce structured catalyst arrays. The model catalytic reactor systems that will be showcased are innovatively employed in industrially relevant chemical reactions for CO₂ conversion and utilisation.¹ Examples of 3D printed monolithic multi-channel systems were developed using co-printed supports and metal catalysts to improve organic chemical synthesis.

One such system under study was based on graphene-oxide (GO) based 3D structured catalysts that were produced using a sustainable, rapid, chemical synthesis route combining the unique properties of graphene and active nanocomposite particles for CO₂ conversion to propylene carbonate.²

The initial results of this study on representative reactions are promising as no separation of the catalyst from the product was needed (with no leeching of the catalyst from the support). In addition to catalytic testing, a combination of conventional characterisation and advanced imaging techniques at multiple resolutions were used, such as new fast XRD-CT tools for simultaneous data collection and analysis allowing for chemistry and physical form to be imaged under preparation and operando conditions.³ The catalysts' pertinent morphological and chemical information can be fed back into the development of the catalyst geometries.

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² Middelkoop, V., Slater, T., Florea, M., Neațu, F., Danaci, S., Onyenkeadi, V., Boonen, K., Saha, B., Baragau, I-A., Kellici, S. (2019). Next frontiers in cleaner synthesis: 3D printed graphene-supported CeZrLa mixed-oxide nanocatalyst for CO₂ utilisation and direct propylene carbonate production. *Journal of Cleaner Production*, 214, pp. 606-614.

³ Vamvakeros. A., Jacques, S.D.M., Di Michiel, M., Matras, D., Middelkoop, V., Ismagilov, I.Z., Matus, E.V., Kuznetsov, V.V., Drnec, J., Senecal, P., Beale, A.M. (2018). 5D operando tomographic diffraction imaging of a catalyst bed, *Nature Comm*, 9, 4751

T4: Smectitic clays as clean and cost effective heterogeneous catalysts

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As the World shifts to a greener more sustainable future, processes and reagents the chemical industry have depended upon for years are increasingly under greater scrutiny. One approach to the challenge of finding better ways of producing the same quality is to look to past catalyst technologies that have fallen out of favor in recent years. Clay, more specifically montmorillonite, based catalysts have been used for many years as clean, cost effective solid Lewis or Brønsted acid catalysts. At low moisture contents, the ionising effect of the charged calcium montmorillonite surfaces can generate Hammett acidities of -3^1 . Acid activation can push the Hammett acidities to as low as -8 as well as open up potent Al^{3+} and Fe^{3+} Lewis acid sites. Said acidified montmorillonites have been reported as being excellent catalysts for a range of reactions, including but not limited to: Friedel-Crafts alkylation², esterification^{3,4}, dehydration⁵, siloxane equilibration⁶ and Diels-Alder cyclo-addition⁷. In addition to their inherent catalytic properties smectitic clays have the potential to be used as supports for reactive ionic or crystalline metal centres through such preparative techniques as intercalation, pillaring or reductive seeding of metal nano-particles.

In this presentation, we firstly detail the performance of FULCAT[®] acid activated clay catalysts in Friedel-Crafts nonylation of diphenylamine (DPA), polymerisation of cyclic siloxanes and esterification reactions. These reactions were chosen due to their commercial importance; nonyl-DPA (nDPA) is sold as a high performance anti-oxidant for car engine lubricants, low molecular weight siloxane polymers are used as building blocks in the production of surfactants and the esterification reaction is one of the cornerstones of organic chemistry. In all reactions, FULCAT[®] catalysts displayed exemplary performance compared to alternative acidified clay catalysts and were extractable from the final product by simple filtration. High performance liquid chromatography (HPLC) was used to describe the nonylation reaction rates, where FULCAT[®] catalysts outperformed alternative solid catalysts and showed good recyclability. Compared to those produced using the traditional Friedel-Crafts Lewis acid catalyst aluminium trichloride ($AlCl_3$) the final FULCAT[®] catalysed nDPA products were optically clear, free of toxic catalyst residues and substituted at the preferred para-position⁸. Polymerisation of cyclic siloxanes proceeded by FULCAT[®] catalysed Si-O bond breakage/reformation equilibration. The extent of reaction was determined by simple viscosity measurements, with FULCAT[®] catalysts again showing excellent efficiency. Two esterification reactions were investigated: the simple esterification of benzoic acid and pentan-1-ol and the ring opening polymerisation of caprolactone. In both reactions, the FULCAT[®] catalysts were benchmarked against the homogeneous toluene sulphonic acid (TSA) catalyst. The esterification of benzoic acid and pentan-1-ol was performed using Dean-Stark apparatus; the reaction was monitored by ¹H NMR and mass water released. FULCAT[®] catalysts were slightly less effective per unit mass than the TSA catalyst but added value to the process by virtue of not having to neutralise the residual organo-acid in the product. Both the TSA and FULCAT[®] catalysts catalysed the side dimerisation of pentan-1-ol reaction. FULCAT[®] catalysts showed good efficiency as a catalyst

for the polymerisation of caprolactone, but the moisture content in the clay catalyst reduced molecular weight and end-group control in the final product.

In the final part of presentation we briefly explore the opportunities for clays as scaffolds for metal nano-particles. Inspired by the work of Varade et al⁹ we repeated a simple method to generate synthetic clay-platinum black nano-composites. The synthetic hectorite LAPONITE[®] auto initiated the reduction of Pt²⁺ from a solution of potassium tetrachloroplatinate to form nano-crystals of platinum black bound to the surface. Commercial opportunities for this new composite material are still to be identified.

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T5: Sustainable nitrogen-doped carbons in hydrogenation reactions

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Catalysed chemical transformations in the liquid phase are a critical component of the continuing elaboration of Power-to-X and Biorefinery concepts. Hydrothermal Carbonisation (HTC)¹ is a sustainable technique that has potential to synthesise tunable and functional nanomaterials that can be applied as catalyst supports in catalysed chemical reactions. HTC materials can be prepared from biomass-derived sugars in the presence of albumin² known to generate promisingly structured porous carbons and opening the possibility of structural nitrogen doping. In this context, our work focuses on nitrogen-doped carbon supports (NDC) which were prepared via HTC and then thermally carbonised at different temperatures in order to direct surface chemistry and nitrogen-containing motifs. The prepared supports were then subsequently impregnated with metal nanoparticles. These catalysts were applied for the hydrogenation of phenol to cyclohexanone in aqueous phase, which is an intermediate for the lignin-to-nylon production. Unique material properties of nitrogen-doped materials affect catalyst selectivity, activity and stability for the hydrogenation of phenol to cyclohexanone. Advantages of this catalyst with regard to catalyst stability and reusability will be demonstrated in comparison to the commercial Pd/AC catalyst.

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T6: Designing catalysts for cascade transformations

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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 reached¹. Cascades offer great advantages in respect of 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. Such highly desirable ‘one-pot’ catalytic cascades necessitate the spatial separation of each catalytic step. Here we describe a general route to a new class of spatially orthogonal (i.e. mutually exclusive) bifunctional porous materials², via stepwise detemplation/functionalisation of a hierarchically interconnected silica framework, which permits the chemical environment of macropores and mesopores to be independently tuned. The hierarchical nature of our pore networks regulates active site accessibility and communication between different spatially localised catalytic functionalities.

Spatial compartmentalization of 2.4 nm Pt NPs within hydrophilic mesopores and 5.5 nm Pd NPs within hydrophobic macropores was verified by HAADF-STEM imaging (Fig. 1) and tomography, and EDX. The catalytic advantage of spatially segregating Pt NPs within mesopores, accessible through interconnected Pd containing macropores, is demonstrated for the cascade selective oxidation of cinnamyl alcohol → cinnamaldehyde → cinnamic acid (Fig. 1), the latter an important flavouring. Pd is selective towards cinnamyl alcohol oxidation to cinnamaldehyde but promotes decarbonylation of the aldehyde product; in contrast, Pt favours undesired hydrogenation of cinnamyl alcohol via reactively-formed surface hydrogen but is highly selective for cinnamaldehyde oxidation to the desirable cinnamic acid product. Spatial compartmentalization within separate but interconnected pore networks, permits control over the reaction sequence, conferring an order of magnitude enhancement in cinnamic acid yield.

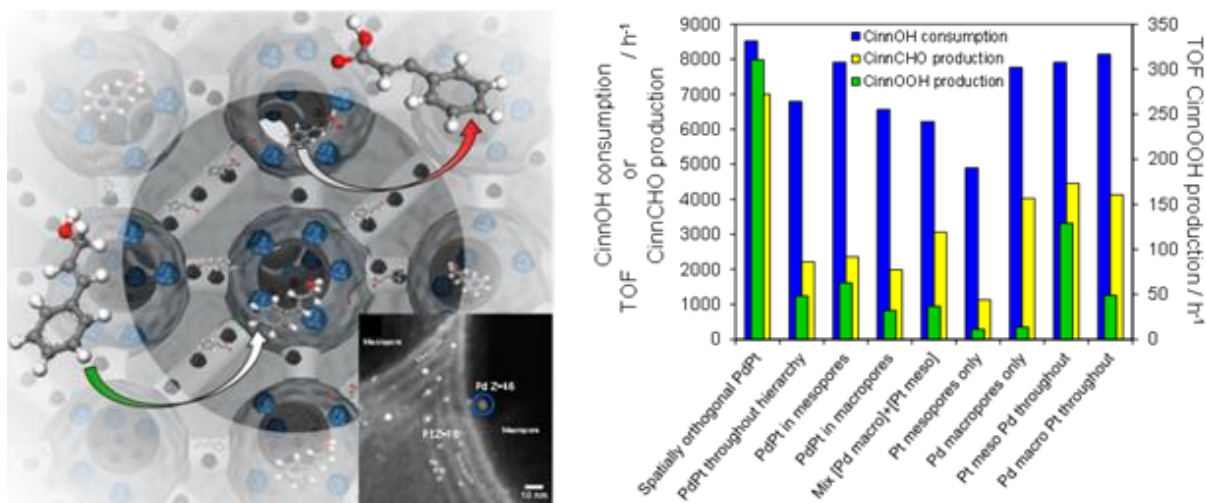


Figure 1 (left) Spatially orthogonal catalysts, with inset HAADF-STEM image and (right) Catalytic cascade aerobic selective oxidation.

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