

Johnson Matthey Academic Conference 2009

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The annual Johnson Matthey Academic Conference was held on 6th and 7th April 2009 at Holywell Park, Loughborough, UK. Attendance at these conferences is by invitation only and the principal aim is to stimulate discussion and encourage exchange of information and ideas between Johnson Matthey's technical teams and the students and academics being supported by the company.

Both days of the conference were opened with a Plenary Lecture by an eminent speaker, followed by a session of technical presentations by students. These technical sessions covered a wide array of topics, such as catalyst preparation and characterisation, nanoparticles and nanotechnology, computational chemistry, emissions control, chemical engineering and fuel cell technology.

Plenary Lectures were given by Professor Chris Hardacre (CentaCat, Queen's University, Belfast, UK) and Professor Lynn Gladden (Department of Chemical Engineering and Biotechnology, University of Cambridge, UK). Both lectures concentrated on different aspects of the recently completed 'Controlling the Access of Reactant Molecules to Active Centres' (CARMAC) Programme. This was an integrated collaborative programme of predominantly Engineering and Physical Sciences Research Council, UK (EPSRC)-funded research between Queen's University, Belfast, University of Reading and University of Cambridge, UK; University of Virginia, USA; Johnson Matthey Plc and Robinson Brothers Ltd, UK.

The principal aim of the CARMAC project was to understand heterogeneous catalysis kinetics at the molecular level through both theoretical modelling and experimental data. This improved understanding should then enable the design of optimised catalytic systems at the plant scale.

Reactions in the Liquid Phase

Professor Chris Hardacre opened proceedings with a keynote address on 'Reactions in the Liquid Phase'. The presentation concentrated on hydrogenation and dehydrogenation reactions.

The transformation of tetrahydrocarbazole to carbazole in the liquid phase over palladium-based catalysts was discussed using results from both dehydrogenation experiments and theoretical computational analysis (1). The preparation of carbazole derivatives is highly important since they have valuable medicinal properties (such as antitumour, antimicrobial and anti-HIV activities) as well as being important materials for the production of agrochemicals, dyes, pigments and optical devices.

A combination of density functional theory (DFT) modelling (Figure 1) and kinetic isotope experiments has led to an enhanced understanding of the dehydrogenation mechanism, with the initial hydrogen abstraction found to be the step with the highest activation energy over a Pd/Al₂O₃ catalyst (2).

The addition of gas-phase hydrogen acceptors (such as alkenes) allowed the equilibrium to be shifted in favour of desired product formation over a Pd/Al₂O₃ or Pd/C catalyst (3). For example, the addition of ethene, propene and but-1-ene resulted in up to a five-fold increase in reaction rate.

Professor Hardacre also described the liquid phase hydrogenation/hydrogenolysis of disulfides over palladium catalysts supported on charcoal (4). It is commonly perceived that sulfur poisoning of platinum group metal catalysts makes this class of reaction impractical. However, it was demonstrated, by using both experimental and theoretical data, that the hydrogenation of sulfur-containing compounds over a Pd catalyst could be successfully achieved (Figure 2). The catalyst could even be recycled under

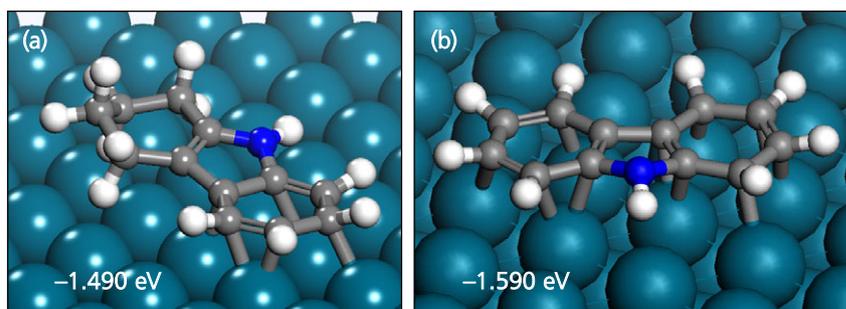


Fig. 1. Density functional theory (DFT) calculations of: (a) tetrahydrocarbazole and (b) carbazole binding on a palladium(111) plane

(Fig. 1(a) Reprinted from (2), with permission from the American Chemical Society; Fig. 1(b) Courtesy of Professor Chris Hardacre)

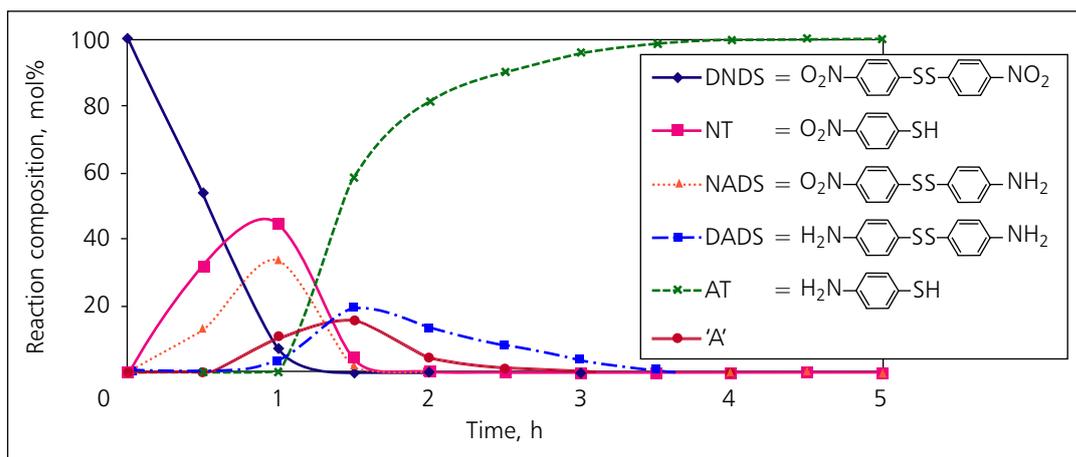


Fig. 2. Reaction profile of the hydrogenation of 4,4'-dinitrodiphenylsulfide over a Pd/Al₂O₃ catalyst. DNDS = 4,4'-dinitrodiphenylsulfide, NT = 4-nitrothiophenol, NADS = 4-nitro-4'-aminodiphenylsulfide, DADS = 4,4'-diaminodiphenylsulfide, AT = 4-aminothiophenol, 'A' = dinitrosodiphenylsulfide (Reprinted, with minor adaptation, from (4) with permission from Elsevier)

relatively mild reaction conditions (hydrogen gas pressure <5 bar).

Throughout his talk, Professor Hardacre demonstrated the power of combining theoretical calculations with experimental data. This allows a full and comprehensive understanding of catalytic systems to be obtained. In order for industry to realise significant benefits from this fundamental chemical knowledge it is vital that real-life applications continue to be studied in collaboration with chemical engineers and computational chemists.

Building a Measurement Platform for Catalysts and Reactors

Day two opened with a keynote address by Professor Lynn Gladden, entitled 'Magnetic Resonance Research Centre: Past, Present and Future – Working with Johnson Matthey'. This focused on applying magnetic resonance imaging (MRI) techniques, developed in the laboratory, to solve real problems faced by scientists and engineers aiming to scale up processes in industry.

It is commonly accepted that catalysts which exhibit high selectivities and activities on the gram scale may not perform to their optimum when the catalyst is formed into larger pellets and packed into a reactor. It is difficult to examine all of the potential reasons for this underperformance, especially when the catalysts are operating in closed industrial reactor systems at high pressures and temperatures. One way to overcome this problem is to use MRI to investigate the system.

MRI is an imaging technique used primarily in medical settings to produce high quality, non-invasive images of the inside of the human body. The MRI scanner uses a powerful magnetic field to align the nuclear magnetisation of (typically) the hydrogen atoms of water molecules in the body. The variation in relaxation times of protons in water in different environments can be measured and allows detailed images to be acquired (Figure 3). In industrial catalysis, the technique can be applied to ^1H or ^{13}C nuclei associated with organic liquids and gases.

Professor Gladden demonstrated how the hydrogenation and isomerisation reactions of 1-octene over a $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst in a trickle-bed reactor can be followed using ^{13}C distortionless enhancement by polarisation transfer (DEPT)-MRI (5) (Figure 4). Trickle-bed reactors are widely used in the petroleum, chemical and waste treatment industries, and

understanding how the reactants are interacting inside is of great interest. Their performance can be closely linked to the flow fields of the fluids within the catalyst bed (6). Inhomogeneities within the packing structure can cause significant local variation in the liquid holdup, wetting and fluid velocities, and in turn, these can impact on the catalyst performance.

Professor Gladden went on to demonstrate the use of similar techniques to investigate the behaviour of liquids inside catalyst pellets. Using a technique known as pulsed-field gradient nuclear magnetic resonance (PFG-NMR), it is possible to measure the diffusion coefficients both inside and outside the ruthenium-on-silica catalyst pellets. The relative rates of diffusion of the reactants and products can have a large impact on the catalyst performance (7). All the data collected with MRI techniques can be used to validate standard computational fluid dynamics techniques and can be used to help design improved reactors and catalyst pellets.



Fig. 3. Sagittal magnetic resonance imaging (MRI) image of a human head (Courtesy of the Oxford Centre for Functional MRI of the Brain, Department of Clinical Neurology, University of Oxford, UK)

The final part of Professor Gladden's talk concentrated on the study of catalysts for alkane dehydrogenation, and probing the catalysts using the relatively new technique of terahertz (THz) time-domain spectroscopy (terahertz radiation is in the far infrared region of the electromagnetic spectrum, from approximately 0.1–20.0 THz, with most work being carried out between 0.5–5.0 THz). In this technique, a short

THz pulse created by a laser passes through the sample and electro-optic detection generates the THz spectrum (more detail on the technique can be found in (8)). Further use of this new spectroscopy technique was shown for the characterisation of different forms of carbon, such as nanotubes and nanofibres.

The relationship between the University of Cambridge and Johnson Matthey has shown how academics and industrialists can work together to develop techniques that are useful in solving real technical problems. However, it was pointed out that a beneficial return is rarely achieved quickly, and it was thought that such collaborations need to be long-term (of at least five years' duration) to be truly effective.

Short Talks and Poster Prizes

There were also a number of short talks and a poster session in which doctoral students presented their latest research. A prize was awarded for the best overall talk given by a student and this went to Sarah Burton (née Hudson) (University of Southampton, UK; now working at Johnson Matthey Fuel Cells, Swindon, UK) for her talk entitled 'A Comparative Study of Alloys and Platinum for Fuel Cell Applications'. Burton described the challenges facing

the commercialisation of fuel cell vehicles and the ways in which alloying with cobalt has resulted in increases in activity (9) and improved stability (10) for fuel cell cathode catalysts. She also showed how a greater understanding of these phenomena could be obtained using X-ray absorption spectroscopy (XAS) (11). Using this technique, the study of structural changes in the catalyst can now be observed during fuel cell operation.

Prizes for the best posters were also awarded, with Paul Rounce (University of Birmingham, UK) winning the second year prize with his poster 'Speciation of Particulate Matter (PM) from Compression Ignition Engines for a Range of Fuels and Biofuels', and Haibo E (University of Oxford, UK) taking the first year prize with her poster entitled 'Custom Microscopy Techniques for Imaging of Core-Shell Catalyst Particles'.

Concluding Remarks

The JMAC 09 conference was deemed a huge success with a high standard of technical presentations and posters that stimulated much debate. Such events have proved mutually beneficial for both academics and industrialists in approaching and tackling key global challenges.

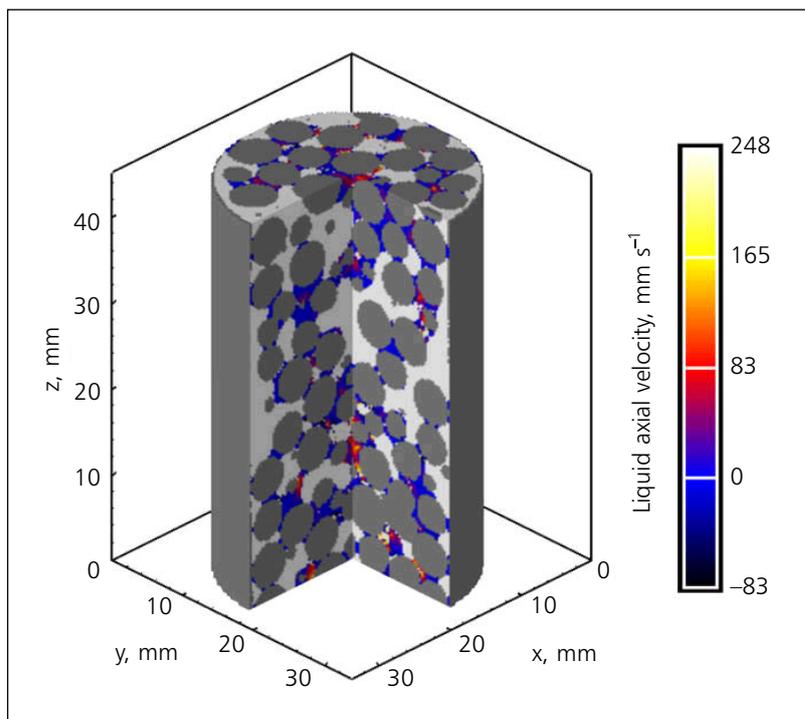


Fig. 4. Three-dimensional DEPT-MRI liquid velocity map of liquid flow in a trickle-bed reactor. The packing elements and the gas-filled void space are shown as dark and light grey areas, respectively (Reprinted from (6), with permission from Elsevier)

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The Reviewers



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James Cookson is a Senior Scientist, also at JMTC, Sonning Common. James obtained a DPhil in Inorganic Chemistry at the University of Oxford, UK, in 2004. After working at the Engineering and Physical Sciences Research Council, he joined Johnson Matthey in 2005. His main interests are the synthesis of precious metal nanoparticles and their application in heterogeneous catalysis for fine chemical and pharmaceutical applications.