

## Johnson Matthey Highlights

### A selection of recent publications by Johnson Matthey R&D staff and collaborators

#### EMISSION CONTROL TECHNOLOGIES

##### Magnetic Resonance Velocity Imaging of Gas Flow in a Diesel Particulate Filter

N. P. Ramskill, A. P. E. York, A. J. Sederman and L. F. Gladden, *Chem. Eng. Sci.*, 2017, **158**, 490

The gas flow in a DPF with sulfur hexafluoride (SF<sub>6</sub>) being used as the magnetic resonance (MR)-active gas was studied by MR velocity imaging. Pictures of the axial velocity were taken at ten evenly spaced places along the length of the filter, for three flow positions corresponding to Reynolds number of Re = 106, 254 and 428 in the filter channels. The averaged axial and through-wall velocity, as a function of place along the length of the filter from the velocity pictures, have been acquired. These experimentally attained velocity profiles were studied and a qualitative comparison with the results of already published numerical simulations was made.

##### Ammonia Mobility in Chabazite: Insight into the Diffusion Component of the NH<sub>3</sub>-SCR Process

A. J. O'Malley, I. Hitchcock, M. Sarwar, I. P. Silverwood, S. Hindocha, C. R. A. Catlow, A. P. E. York and P. J. Collier, *Phys. Chem. Chem. Phys.*, 2016, **18**, (26), 17159

In commercial NH<sub>3</sub>-SCR catalyst the diffusion of NH<sub>3</sub> was measured and compared with H-CHA by quasielastic neutron scattering (QENS) and molecular dynamics (MD) simulations, and the effect of counterion presence on NH<sub>3</sub> mobility in automotive emission control relevant zeolite catalysts was assessed. Jump diffusion with a jump distance of 3 Å was given by QENS and over the measured temperature range provides comparable self-diffusion coefficient measurements for both Cu- and H-CHA samples in the range of ca. 5–10 × 10<sup>-10</sup> m<sup>2</sup> s<sup>-1</sup>. MD was used to calculate self-diffusivities which were within a factor of 6 of those measured experimentally at each temperature. The activation energies of diffusion: 3.7 and 4.4 kJ mol<sup>-1</sup> for H- and Cu-chabazite respectively, were similar, indicating that counterion presence has little influence on NH<sub>3</sub> diffusivity on the timescale of the QENS experiment. The MD simulations reveal strong

coordination of NH<sub>3</sub> with Cu<sup>2+</sup> counterion in the centre of the chabazite cage which shields other molecules from interacting with the ion and enables intercage diffusion through the 8-ring windows to continue unhindered.

##### Impact of Rh Oxidation State on NO<sub>x</sub> Reduction Performance of Multi-Component Lean NO<sub>x</sub> Trap (LNT) Catalyst

J. Li, N. Currier, A. Yezerets, H.-Y. Chen, H. Hess and S. Mulla, *SAE Int. J. Engines*, 2016, **9**, (3), 1615

The redox history of commercial LNT catalysts was found to play a role in determining NO<sub>x</sub> conversion under lean/rich cycles. Pre-reduced LNT catalyst showed much better NO reduction during temperature-programmed reduction of NO compared to oxidised LNT catalyst. By studies with Rh-only and Pt-only catalyst, Rh was demonstrated to be the determining factor in variation of the NO reduction function due to oxidation state change. Kinetic analysis was carried out to study the mechanism, and NO reduction over reduced Rh is well described by an Arrhenius equation with first-order dependence on NO concentration. By contrast, the surface redox state of the oxidised catalyst changed during NO reduction. The activation energy of NO reduction over reduced fully formulated LNT catalyst was found to be ~180 ± 14 kJ mol<sup>-1</sup>.

#### NEW BUSINESSES: BATTERY TECHNOLOGIES

##### Synthesis and Thermophysical Properties of Ether-Functionalized Sulfonium Ionic Liquids as Potential Electrolytes for Electrochemical Applications

E. Coadou, P. Goodrich, A. R. Neale, L. Timperman, C. Hardacre, J. Jacquemin and M. Anouti, *Chem. Phys. Chem.*, 2016, **17**, (23), 3992

A new series of hydrophobic room temperature ionic liquids (ILs) based on five ether functionalised sulfonium cations with bis{(trifluoromethyl)sulfonyl}imide, [NTf<sub>2</sub>]<sup>-</sup> anion have been prepared and characterised. Their density, viscosity, ionic conductivity, electrochemical window, phase transition behaviour and decomposition temperature have been measured. Each of the new ILs had a large liquid temperature range, low viscosity and good conductivity. DFT calculations and electrochemical

characterisation studies have also demonstrated good electrochemical stability windows. The ILs could be suitable for use as electrolyte materials in lithium batteries and capacitors.

## PROCESS TECHNOLOGIES

### Techniques for Direct Experimental Evaluation of Structure–transport Relationships in Disordered Porous Solids

A. Nepryahin, R. S. Fletcher, E. M. Holt and S. P. Rigby, *Adsorption*, 2016, **22**, (7), 993

Assessing structure-transport relationships is vital to optimising the activity and selectivity performance of porous pellets acting as heterogeneous catalysts for diffusion-limited reactions. The determination of the impact of specific aspects of the void space on mass transport for amorphous porous systems usually requires complex characterisation and modelling steps to deconvolve the precise impact of the feature in question. There is little accuracy and precision in these characterisation and modelling steps. In this study the authors demonstrate the use of a more direct experimental analysis of the impact of pore network features on mass transport. The efficacy of the macropores of a bidisperse porous foam structure on improving mass transport over a purely mesoporous system was evaluated.

### Oxidation of Cinnamyl Alcohol using Bimetallic Au–Pd/TiO<sub>2</sub> Catalysts: A Deactivation Study in a Continuous Flow Packed Bed Microreactor

G. Wu, G. L. Brett, E. Cao, A. Constantinou, P. Ellis, S. Kuhn, G. J. Hutchings, D. Bethell and A. Gavriilidis, *Catal. Sci. Technol.*, 2016, **6**, (13), 4749

The authors assessed the stability of 1% bimetallic Au-Pd (5:95)/TiO<sub>2</sub> catalyst in a packed bed capillary microreactor for oxidation of cinnamyl alcohol. Different reaction conditions were studied: 80–120°C, oxygen concentration 0–100% and total pressure 4 bara. Cinnamaldehyde, 3-phenyl-1-propanol and *trans*- $\beta$ -methylstyrene were the main products observed. Whilst the same catalyst has good stability in the oxidation of benzyl alcohol, it deactivated during the oxidation of cinnamyl alcohol, especially at high reaction temperatures. Improved cinnamaldehyde selectivity was observed with a higher concentration of oxygen used for the reaction but lower conversion and higher deactivation rates. A fraction of the activity was recovered by treatment with hydrogen. Pd leaching and a complex effect of oxygen caused the deactivation.

### Retrosynthetic Co-Templating Method for the Preparation of Silicoaluminophosphate Molecular Sieves

A. Turrina, R. Garcia, P. A. Cox, J. L. Casci and P. A. Wright, *Chem. Mater.*, 2016, **28**, (14), 4998

Synthesis methods for target zeotypes of the ABC-6 structural family containing *gme* cages have been designed using a retrosynthetic method. Silicoaluminophosphate versions of AFX (SAPO-56), SFW (STA-18), and GME (STA-19) topology types were created. The method promotes formation of desired structural features using two organic structure-directing agents, identified by computational modelling. The *gme* cage was obtained using a trimethylammonium cation and additional cages or channels could be directed using bisdiazabicyclooctane (DABCO) alkane cations and quaternary ammonium oligomers of DABCO with connecting polymethylene chain lengths of 4–8 methylene units. SAPO-56, STA-18 and some of the STA-19 materials were calcined to produce microporous, tetrahedrally coordinated framework solids with AFX, SFW and GME topologies. Other STA-19 samples converted topotactically to SAPO-5.

### The Cluster Beam Route to Model Catalysts and Beyond

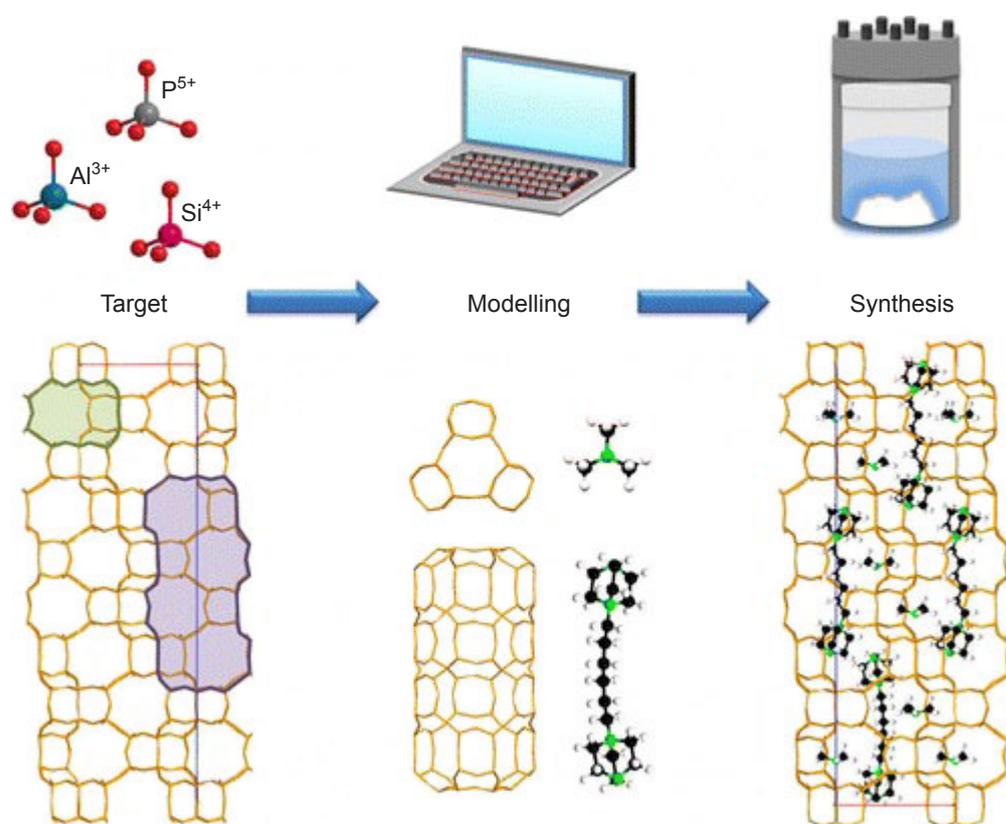
P. R. Ellis, C. M. Brown, P. T. Bishop, J. Yin, K. Cooke, W. D. Terry, J. Liu, F. Yin and R. E. Palmer, *Faraday Discuss.*, 2016, **188**, 39

After an intermediate mass filtering step, generating beams of atomic clusters in the gas phase and their following deposition (in vacuum) onto appropriate catalyst supports, represents a potential and attractive method for preparing model catalyst particles. The nanocluster beam method has several benefits compared with the colloidal process to producing preformed catalytic nanoparticles: the clusters created in the beam have no ligands, their size can be chosen to arbitrarily high precision by the mass filter and metal particles consisting of challenging compositions of metals can be easily produced. Until now the distinctly low rates of metal particle production of the order of 1 microgram per hour, has held back the cluster method. This is a few orders of magnitude below what is preferable for research-level reaction research under realistic conditions but this is more than enough for surface science research. The authors examine solutions to this scaling issue, in particular, the development of two new generations of cluster beam sources which propose that cluster beam yields of grams per hour may eventually be viable.

### Visible Light Photocatalysis by Metal-to-metal Charge Transfer for Degradation of Methyl Orange

C. P. Ireland, R. G. Palgrave, S. C. Bennett, A. W. J. Smith, J. H. Clark, J. R. Darwent, J. B. Claridge, S. Poulston and M. J. Rosseinsky, *J. Mater. Chem. A*, 2016, **4**, (32), 12479

Bulk oxide-oxide interfaces were made by impregnating chromium(III) onto a high surface area particulate niobium oxide and the precise energy of the metal-to-metal charge transfer transition that is accountable for the visible light photocatalytic



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decomposition of methyl orange is determined by a combination of X-ray photoelectron spectroscopy and diffuse reflectance.

#### PFG NMR and Bayesian Analysis to Characterise Non-Newtonian Fluids

T. W. Blythe, A. J. Sederman, E. H. Stitt, A. P. E. York and L. F. Gladden, *J. Magn. Res.*, 2017, **274**, 103

NMR is a non-invasive technique that can be applied for investigating changes in the rheological behaviour of process fluids that affect industrial flow processes. Results can be obtained online, or inline, and used for process control and optimisation over timescales of minutes or less, without optical opacity limits. This paper presents a Bayesian analysis approach using pulsed field gradient (PFG) NMR to estimate the rheological parameters of Herschel-Bulkley fluids. The robustness of the proposed approach was studied using simulated noisy NMR data and reduced sampling, demonstrating that even with a signal-to-noise ratio (SNR) of 100, as few as 16 sampled points can provide rheological parameters accurate to within 2% of the ground truth. Experimental validation was carried out through an experimental case study on model Herschel-Bulkley fluids. The results took a total acquisition time of <60 s representing an 88% reduction in acquisition time compared to MR flow imaging.

#### Arene Guest Selectivity and Pore Flexibility in a Metal–Organic Framework with Semi-Fluorinated Channel Walls

R. Smith, I. J. Vitorica-Yrezabal, A. Hill and L. Brammer, *Phil. Trans. Roy. Soc. A*, 2017, **375**, (2084), 20160031

A MOF with 1D channels of approximately hexagonal cross-section [ $\text{Ag}_2(\text{O}_2\text{CCF}_2\text{CF}_2\text{CO}_2)(\text{TMP})$ ] (TMP = 2,3,5,6-tetramethylpyrazine) was synthesised with MeOH filling the channels in its as-synthesised form. Alternating columns of Ag(I) centres are connected by two ligand types around the channels and along their length, producing an alternating arrangement of hydrocarbon (C–H) and fluorocarbon (C–F) groups lining the channel walls. The C–H groups project further into the channel than the C–F groups. In the channels MeOH can be exchanged for a variety of arenes including xylenes and tetrafluorobenzene, and these results were confirmed by various spectroscopic techniques. Alkanes and perfluoroalkanes were not found to enter the channels. The evacuated MOF was not stable for more than a few minutes under ambient conditions or when heated. An irreversible solid-state transformation to a non-porous polymorph comprising  $\text{Ag}_2(\text{O}_2\text{CCF}_2\text{CF}_2\text{CO}_2)$  coordination layers pillared by TMP ligands was observed under these circumstances.

## Engineering Aspects of Hydrocarbon Steam Reforming Catalysts

P. W. Farnell, *Top. Catal.*, 2016, **59**, (8), 802

This article describes the engineering challenges of steam reforming catalysts and their future development trends. Steam reforming is the main route to produce synthesis gas, the key intermediate in the manufacture of chemicals such as ammonia, methanol and acetic acid. It has been used to make transportation fuels *via* Fischer-Tropsch, and could be a route towards clean energy. The catalysts have been optimised for improved plant reliability, lower capital costs and maximised thermal efficiency. Standard industrial operating conditions have been in use successfully for many years with little development in terms of catalysis, while most of the development has been on the macro scale engineering performance and in the steam reforming reactors.