

# Johnson Matthey Highlights

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

## EMISSIONS CONTROL TECHNOLOGIES

### Enhancing the Low Temperature Oxidation Performance over a Pt and a Pt-Pd Diesel Oxidation Catalyst

J. M. Herreros, S. S. Gill, I. Lefort, A. Tsolakis, P. Millington and E. Moss, *Appl. Catal. B: Environ.*, 2014, **147**, 835

Hydrogen has been reported to have a positive effect on the oxidation kinetics of CO, HC and NO over Pt and Pt-Pd DOCs. The aim of this work was to determine whether this effect is due to the temperature rise during hydrogen oxidation or a change in reaction kinetics due to the influence of intermediate species. The research suggests that small amounts of hydrogen improve catalyst light-off and also promote NO oxidation over both catalyst types. The authors claim these benefits are due to both exothermic reactions increasing local catalyst temperatures, and also a result of hydrogen increasing reaction rates and accessibility to catalyst active sites therefore promoting CO, HC and NO oxidation at lower temperatures.

### HCN Emissions in Fluid Catalytic Cracking

M. O. Xunhua, B. De Graaf and P. Diddams, *Petroleum Technol. Quarterly*, 2013, **18**, (2), 81

FCC reactors are common components in refineries around the world with these reactors being fed with either heavy streams from other refinery units or other low-value components. By their nature these feeds contain a large number of contaminants, such as heavy metals and heteroatoms like S and N, which must be removed in order to meet emissions regulations; recently HCN has fallen under scrutiny in the USA and therefore added to the existing restrictions of SO<sub>x</sub>, NO<sub>x</sub> and particulate emissions from these reactors. This research evaluates the trade-off between HCN and NO<sub>x</sub> emissions and highlights that flue gas emissions control is a combination of factors arising from both the choice of additive and the design of the regenerator unit.

## PROCESS TECHNOLOGIES

### Use of an Areal Distribution of Mixing Intensity to Describe Blending of Non-Newtonian Fluids in a Kenics KM Static Mixer Using PLIF

F. Alberini, M. J. H. Simmons, A. Ingram and E. H. Stitt, *AIChE*, 2014, **60**, (1), 332

The blending of Newtonian and time-independent non-Newtonian fluids in KM static mixers was evaluated using PLIF. The effect of a number of mixing parameters, fluid rheology and apparent viscosity ratio was investigated for two-fluid blending conducted at constant superficial velocity (0.3 ms<sup>-1</sup>) and measured from images taken at the mixer outlet after introducing a stream of dye at the inlet. The PLIF images were analysed to determine the log variance and maximum striation thickness and this revealed conflicting trends. It was found that for two-fluid blending the PLIF image showed unmixed spots of a high viscosity material when introduced into a lower viscosity component.

### Characterization of Au<sup>3+</sup> Species in Au/C Catalysts for the Hydrochlorination Reaction of Acetylene

M. Conte, C. J. Davies, D. J. Morgan, A. F. Carley, P. Johnston and G. J. Hutchings, *Catal. Lett.*, 2014, **144**, (1), 1

The preparation of a set of Au/C catalysts for the gas phase hydrochlorination of acetylene to vinyl chloride monomer was carried out using a range of impregnation solvents and variation of the drying temperature. A range of strong acids were evaluated as impregnation solvents and the use of *aqua regia* in combination with an intermediate drying temperature of 140°C resulted in the most active catalyst. XPS and TPR were used to evaluate the effects of the catalyst preparation parameters on catalytic activity and thermal reduction methods in particular were found to assist with the determination of the kinetic parameters for the reduction of Au<sup>3+</sup> to Au<sup>0</sup> using hydrogen.

### Catalytic Syngas Purification from Model Biomass Gasification Streams

A. M. Steele, S. Poulston, K. Magrini-Bair and W. Jablonski, *Catal. Today*, 2013, **214**, 74

The production of clean biomass-derived syngas remains an important goal in the commercial manufacture of biofuels. A range of Ni and Rh containing catalysts were evaluated for the conversion of model tar components (toluene and naphthalene or benzene) in a simulated biogas feed containing up to

100 ppm H<sub>2</sub>S and 5 vol% CH<sub>4</sub> at temperatures between 700°C and 900°C. H<sub>2</sub>S was found to significantly reduce hydrocarbon conversion but near complete conversion of CH<sub>4</sub> and tar could be achieved on a Rh-based catalyst at 900°C with a very high GHSV of 150,000 h<sup>-1</sup>. At a more realistic GHSV of 60,000 h<sup>-1</sup> and higher CH<sub>4</sub> levels (5 vol%) the effect of H<sub>2</sub>S concentration on catalyst activity followed an apparent linear activity decay law. The catalyst deactivation by H<sub>2</sub>S was found to be fully reversible and attributable to a transient site-blocking mechanism. A selection of catalysts were evaluated for tar and methane conversion using oak modelled syngas and the best candidates were then tested using oak derived syngas generated using a pilot-scale gasification unit. Rh catalysts were found to exhibit the best performance in terms of hydrocarbon conversion when compared to the Ni catalysts under similar conditions. The best Rh catalyst had a methane conversion of 95% over a 200 hour test showing little or no loss of activity when using the oak modelled syngas.

#### Ethane Steam Reforming over a Platinum/Alumina Catalyst: Effect of Sulfur Poisoning

C. Gillan, M. Fowles, S. French and S. D. Jackson, *Ind. Eng. Chem. Res.*, 2013, **52**, (37), 13350

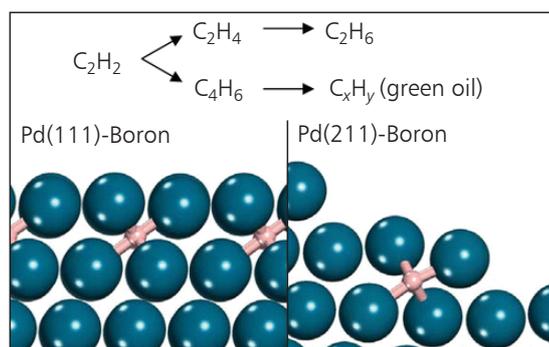
The effect of H<sub>2</sub>S and CH<sub>3</sub>SH as poisons for Pt catalysts during the steam reforming of ethane was evaluated. Both poisons were shown to deactivate the catalyst over a number of hours, but of the two CH<sub>3</sub>SH proved more detrimental, reducing conversion rates almost by an order of magnitude. Selectivity was also affected, showing that the effect of S was not uniform on all reactions occurring over the catalyst and the production of CH<sub>4</sub> was reduced the most, while the water-gas shift reaction was affected to a lesser extent. A slight regeneration of the catalyst was seen upon removal of the CH<sub>3</sub>SH, but no regeneration was observed after removal of H<sub>2</sub>S. Overall, the poisons reduced activity and improved selectivity for hydrogen.

#### Selective Hydrogenation of Acetylene over Pd-Boron Catalysts: A Density Functional Theory Study

B. Yang, R. Burch, C. Hardacre, P. Hu and P. Hughes, *J. Phys. Chem. C*, 2014, **118**, (7), 3664

Density functional theory was used to investigate the hydrogenation of acetylene over B-modified Pd(111) and Pd(211) surfaces. This reaction has exhibited excellent performance experimentally using these catalysts. The selectivity of the reaction for ethylene formation was studied in two ways, firstly a comparison between the desorption and hydrogenation of ethylene and secondly a comparison between the formation

of ethylene and 1,3-butadiene. The formation of sub-surface carbon and hydrogen on these catalysts has also been reported to affect the activity and selectivity of ethylene production from acetylene and the authors also evaluated the formation of these species. The results showed that these B-modified catalysts show similar activity and selectivity to C-modified Pd surfaces, the formation of 1,3-butadiene on the B-modified catalysts was slightly suppressed and the formation of sub-surface carbon and hydrogen was eliminated.



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#### Fundamental Aspects of H<sub>2</sub>S Adsorption on CPO-27-Ni

S. Chavan, F. Bonino, L. Valenzano, B. Civalleri, C. Lamberti, N. Acerbi, J. H. Cavka, M. Leistner and S. Bordiga, *J. Phys. Chem. C*, 2013, **117**, (30), 15615

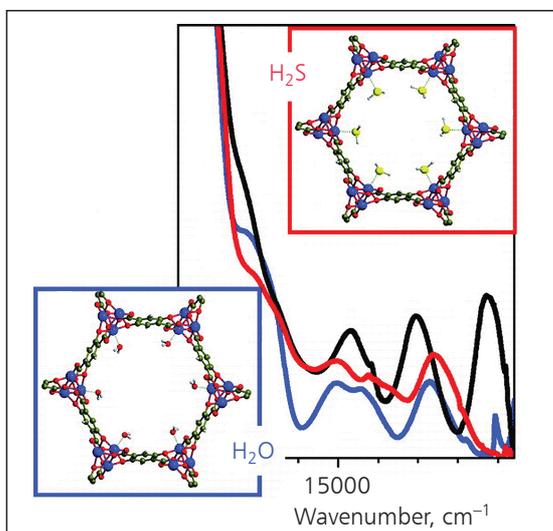
Gas storage in MOFs has been an area of interest for many years both due to their high surface areas and chemical modularity. This research studied the adsorption of H<sub>2</sub>S on Ni<sub>2</sub>(dhtp)(H<sub>2</sub>O)<sub>2</sub>•8H<sub>2</sub>O MOF (known as CPO-27-Ni or MOF-74-Ni) which was characterised using *in situ* PXRD, FTIR, Raman and UV-vis spectroscopy and also by first-principles periodic boundary conditions calculations. The results demonstrated high stability of the MOF in the presence of H<sub>2</sub>S, but a clear colour change was observed in the sample which shows that H<sub>2</sub>S strongly coordinates to the Ni sites in the structure. Good agreement was seen between experimental and computed energies of interaction.

#### New Methods in Biomass Depolymerisation: Catalytic Hydrogenolysis of Barks

M. D. Garrett, S. C. Bennett, C. Hardacre, R. Patrick and G. N. Shelldrake, *RSC Adv.*, 2013, **3**, (44), 21552

The conversion of biomass into useful chemical

feedstocks is of increasing interest in the development of a sustainable chemical industry. This paper looks at the conversion of suberin, a material of low commercial value thought to be responsible for the waterproofing properties of bark. The hydrogenolysis of three species of tree bark (sycamore, spruce and cork) was studied using heterogeneous pgm catalysts and produced two major product streams. The lignin and lignin-like regions of suberin produced aromatic substituted guaiacols and the polyester regions yielded a range of saturated fatty acids and alcohols, including  $\alpha,\omega$ -functionalised species. The authors claim advantages to catalytic hydrogenolysis over conventional base hydrolysis both in terms of selectivity and conversion.



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## NEW BUSINESSES: FUEL CELLS

### Atomic Imaging of Carbon-Supported Pt, Pt/Co, and Ir@Pt Nanocatalysts by Atom-Probe Tomography

T. Li, P. A. J. Bagot, E. Christian, B. R. C. Theobald, J. D. B. Sharman, D. Ozkaya, M. P. Moody, S. C. E. Tsang and G. D. W. Smith, *ACS Catal.*, 2014, **4**, (2), 695

Commercially prepared Pt, Pt/Co alloy, and Ir@Pt core-shell nanoparticles supported on high-surface-area C black were characterised by APT. The internal structures of the nanoparticles were studied using concentration profiles and 3D atom maps and the distribution of trace impurity elements, including Na and Cl, was also examined. The Pt nanoparticle showed

Na was retained on the surface, indicating more rigorous washing may be required during preparation, the Pt/Co system exhibited marked variations in both composition and particle size and the Ir@Pt core-shell particles showed significant intermixing of the metals, an observation which would have been difficult to make using alternative techniques. All of these findings are likely to affect catalytic performance. The authors suggest that the ability of APT to analyse single nanoparticles and provide chemical mapping could provide a means of quality control and that this information could improve the preparation methods for nanoscale catalysts.

### Characterisation of Platinum-based Fuel Cell Catalyst Materials Using $^{195}\text{Pt}$ Wideline Solid State NMR

G. J. Rees, S. T. Orr, L. O. Barrett, J. M. Fisher, J. Houghton, G. H. Spikes, B. R. C. Theobald, D. Thompsett, M. E. Smith and J. V. Hanna, *Phys. Chem. Chem. Phys.*, 2013, **15**, (40), 17195

A novel FSFT method was used to acquire wideline  $^{195}\text{Pt}$  NMR data of Pt nanoparticles and Pt-Sn intermetallics/bimetallics. These nanoparticles can be used to catalyse oxidative reactions in fuel cell applications and the literature in this area of wideline NMR data is dominated by the alternative technique of SEHS (or SEIS). The FSFT method allowed for the mean number of atoms in a Pt nanoparticle to be estimated and also for detailed information about the number of atoms effectively present in each layer from the surface to be determined. The authors compared the FSFT technique to SEHS and saw advantages to using FSFT. Also presented here is the first  $^{195}\text{Pt}$  NMR characterisation of diamagnetic  $\text{Pt}_{13}$  nanoclusters which have no metallic character. This technique allows for a direct measure of isotropic chemical shift and is a better means of measuring the actual Knight shift when compared to referencing against the primary IUPAC shift standard.

### Flame Spray Pyrolysis Generated Transition Metal Oxide Nanoparticles as Catalysts for the Growth of Carbon Nanotubes

F. Dillon, M. Copley, A. A. Koós, P. Bishop and N. Grobert, *RSC Adv.*, 2013, **3**, (43), 20040

The growth of MWCNTs using three transition metal oxide nanoparticles ( $\text{Fe}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$  and NiO) was investigated. Synthesis of the nanoparticles was conducted using FSP and since the syntheses for both the CNT and nanoparticles were identical, a direct comparison of the products was possible allowing for the identification of links between the catalyst

and the morphology of the resultant nanostructures. Conventional CNTs were grown on  $\text{Fe}_2\text{O}_3$  nanoparticles, no discernible growth was detected on  $\text{Co}_3\text{O}_4$  and a mixture of conventional and coiled CNTs was observed on NiO. The authors investigated the effect of temperature, time and acetylene/hydrogen gas mixtures on the morphology, yield and purity of the CNTs and found that the yield of coiled CNTs can be increased to approximately 70% of the CNT yield.