

Johnson Matthey Highlights

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

EMISSION CONTROL TECHNOLOGIES

Understanding the Gas Transport in Porous Catalyst Layers by Using Digital Reconstruction Techniques

V. Novák, M. Dudák, P. Kočí and M. Marek, *Curr. Opinion Chem. Eng.*, 2015, 9, 16

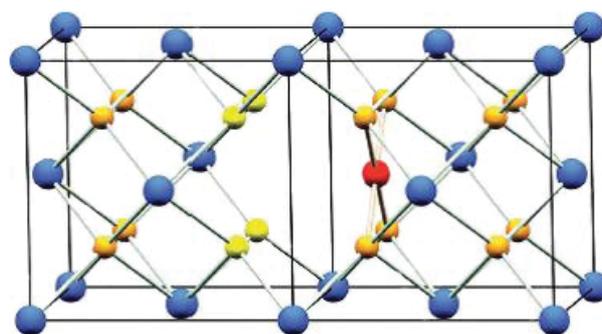
Internal transport limitations are studied in supported porous catalytic layers to understand their effect on the performance of a catalytic reactor, specifically an automotive catalytic converter. The results are considered generally applicable. 3D digital reconstruction and complex mathematical modelling were applied and case studies are presented to illustrate their use in optimising transport properties in a porous supported catalyst.

Incorporation of Square-planar Pd²⁺ in Fluorite CeO₂: Hydrothermal Preparation, Local Structure, Redox Properties and Stability

C. I. Hiley, J. M. Fisher, D. Thompsett, R. J. Kashtiban, J. Sloan and R. I. Walton, *J. Mater. Chem. A*, 2015, 3, (24), 13072

Low-temperature hydrothermal synthesis was used to prepare a number of nanocrystalline Pd-substituted ceria-type fluorites of the form Ce_{1-x}Pd_xO_{2-δ} (0.05 ≤ x ≤ 0.15). Efforts to attain a higher value of Pd substitution results in PdO being formed as a secondary phase. X-ray absorption near edge structure revealed that Ce and Pd were in the +4 and +2 oxidation states respectively, therefore proposing oxide deficiency as the mechanism of charge balance. Pd²⁺ has local square-planar coordination which was confirmed by the extended X-ray absorption fine structure (EXAFS) analysis at the Pd K-edge. A structural model, consistent with earlier modelling investigations, can be fitted in which the mean fluorite structure was kept but with Pd²⁺ sitting in the square faces of oxide ions available in the local cubic geometry of Ce. Pd is well dispersed in the nanocrystalline ceria particles as shown by TEM analysis and *in situ* powder XRD indicated that upon heating in air the samples continue to be stable up to 800°C.

Heavy Duty Emission Control System Analysis and Optimization for Future Demands



C. I. Hiley, J. M. Fisher, D. Thompsett, R. J. Kashtiban, J. Sloan and R. I. Walton, *J. Mater. Chem. A*, 2015, 3, (24), 13072 (Reproduced by permission of The Royal Society of Chemistry)

J. Jansson, Å. Johansson, H. Sjoval, M. Larsson, G. Smedler, C. Newman and J. Pless, *SAE Technical Paper* 2015-01-0997, 2015

This paper, presented at SAE 2015 World Congress & Exhibition, reviews emission control systems for heavy duty diesel (HDD) applications to meet post-EuroVI/US10 legislation. It focuses on systems containing SCR and covers the optimisation of the system for both fuel consumption and catalyst efficiency. Pros and cons are considered and it is concluded that all current legislative requirements may be met using optimised SCR containing systems.

Thermal Decomposition of Bulk and Supported Barium Nitrate

C. J. Bardwell, R. I. Bickley, S. Poulston and M. V. Twigg, *Thermochim. Acta*, 2015, 613, 94

The decomposition of anhydrous bulk barium nitrate to produce O₂ and NO plus small quantities of NO₂, N₂ and N₂O was found to take place principally at 630°C. Lower temperature decomposition took place after dispersing on Al₂O₃ and TiO₂. This procedure also increased the complexity of the decomposition products as well as causing increased N₂O production due to reaction of adsorbed gases on the supports.

FINE CHEMICALS: CATALYSIS AND CHIRAL TECHNOLOGIES

A Halogen- and Hydrogen-bonding [2]catenane for Anion Recognition and Sensing

J. M. Mercurio, A. Caballero, J. Cookson and P. D. Beer, *RSC Adv.*, 2015, 5, (12), 9298

An anion templated Grubbs' II-catalysed RCM clipping mechanical bond forming process was used to synthesise a mixed halogen- and hydrogen-bonding hetero-[2]catenane. The interlocked catenane host was able to bind and sense anions, and form strong associations with acetate and dihydrogen phosphate as shown by ^1H NMR spectroscopy and fluorescence titration experiments.

NEW BUSINESSES: BATTERY TECHNOLOGIES

Transforming Anatase TiO_2 Nanorods into Ultrafine Nanoparticles for Advanced Electrochemical Performance

D. Bresser, G.-T. Kim, E. Binetti, M. Striccoli, R. Comparelli, S. Seidel, D. Ozkaya, M. Copley, P. Bishop, E. Paillard and S. Passerini, *J. Power Sources*, 2015, 294, 406

Although the smaller diffusion pathways for ions and electrons are frequently the main reason for nanostructuring lithium-ion active materials, there are also other, less-expected phenomena happening when leaving the microscale to go into the nanoscale. The authors investigate one of these phenomena – the thermally induced fragmentation (i.e. 'chopping') of oleic acid-capped anatase TiO_2 nanorods perpendicular to the [001] direction. As a result of the fragmentation, ultrafine TiO_2 nanoparticles with improved (001) facets are formed. These ultrafine nanoparticles have a fantastic rate performance and cycling stability, even for cathodic cut-off potentials as low as 0.1 V, due to the altered surface facets ratio and the beneficial utilisation of carboxymethyl cellulose as binder.

NEW BUSINESSES: FUEL CELLS

Properties of the Hydrogen Oxidation Reaction on Pt/C Catalysts at Optimised High Mass Transport Conditions and its Relevance to the Anode Reaction in PEFCs and Cathode Reactions in Electrolysers

C. M. Zalitis, J. Sharman, E. Wright and A. R. Kucernak, *Electrochim. Acta*, 2015, 176, 763

A model is developed for use in simulation studies of fuel cell and electrolyser systems using Pt/C catalyst with ultra-low loadings ($0.84\text{--}3.5\ \mu\text{g}_{\text{Pt}}\ \text{cm}^{-2}$, Johnson Matthey's HiSPEC 9100). The dependence of the hydrogen reaction on pH and H_2 concentration may be understood using this model. Using a high mass transport floating electrode technique allowed features of the HOR and HER to be elucidated for the first time. Fine structure has been resolved in the H_2 adsorption

region and the features correlated to functions of the H_2 and H^+ concentration, anion concentration, potential scan limit and temperature.

PRECIOUS METAL PRODUCTS

A Density Functional Study of Oxygen Vacancy Formation on $\alpha\text{-Fe}_2\text{O}_3(0001)$ Surface and the Effect of Supported Au Nanoparticles

S. W. Hoh, L. Thomas, G. Jones and D. J. Willock, *Res. Chem. Intermed.*, 2015, 41, (12), 9587

The PBE + U calculations of Au nanoparticles supported on the on $\alpha\text{-Fe}_2\text{O}_3(0001)$ surface were investigated and the authors found that the periphery atoms of Au_{10} particles became oxidised *via* the dissociation of O_2 at the metal-oxide interface. The metal particle was shown to significantly decrease the defect formation energy for surface oxygen vacancies in the oxide support especially when the nanoparticle is in a semi-oxidised state. The defect formation energy depends on the distance of the vacancy from the metal particle so the smallest defect formation energies are calculated for oxygen vacancies formed under the Au nanoparticle. For $\text{Au}_{10}/\alpha\text{-Fe}_2\text{O}_3(0001)$ forming the vacancy under the cluster involves a defect formation energy of 2.13 eV (relative to $\frac{1}{2}\text{O}_2(\text{g})$) and this falls to 0.86 eV when the perimeter of the particle is oxidised. These values are substantially less than that for the bare $\alpha\text{-Fe}_2\text{O}_3(0001)$ of 3.04 eV.

PROCESS TECHNOLOGIES

$\text{NiO}/\text{CaAl}_2\text{O}_4$ as Active Oxygen Carrier for Low Temperature Chemical Looping Applications

J. A. Medrano, H. P. Hamers, G. Williams, M. van Sint Annaland and F. Gallucci, *Appl. Energy*, 2015, 158, 86

A commercial Ni-based catalyst has been tested for chemical looping to capture CO_2 more efficiently from chemical processes at low temperature. Its behaviour at low temperature has been investigated and it was found to require pre-treatment at higher reduction temperature as an activation step. The oxygen carrying capacity is thereby increased, improving reactivity. Redox kinetics were found to be adequate for low temperature applications up to 200 cycles. The kinetic rates for gas-phase and gas-solid reactions are also available to use for prediction of performance in such applications.

Effect of Mill Type on the Size Reduction and Phase Transformation of Gamma Alumina

S. R. Chauruka, A. Hassanpour, R. Brydson, K. J. Roberts, M. Ghadiri and H. Stitt, *Chem. Eng. Sci.*, 2015, 134, 774

Air jet milling, planetary ball milling and single ball milling were employed to investigate the effects of stress modes on particle size reduction in γ -alumina, a frequently used catalyst support. The size reduction achieved was

greatest for air jet milling, from a d_{90} of 37 μm to 2.9 μm . Single ball milling produced a size reduction to 10.5 μm . The planetary ball milling procedure gave the least size reduction to 30.2 μm and also caused phase transition to unwanted α -alumina. The shear rates are known to be higher in planetary ball milling compared to other types of milling, and this is thought to account for the differences.

A Kinetic Analysis Methodology to Elucidate the Roles of Metal, Support and Solvent for the Hydrogenation of 4-phenyl-2-butanone over Pt/TiO₂

S. K. Wilkinson, I. McManus, H. Daly, J. M. Thompson, C. Hardacre, N. S. Bonab, J. ten Dam, M. J. H. Simmons, C. D'Agostino, J. McGregor, L. F. Gladden and E. H. Stitt, *J. Catal.*, 2015, **330**, 362

The choice of solvent affects the rate and selectivity (ketone vs. aromatic ring) of the hydrogenation of 4-phenyl-2-butanone over a Pt/TiO₂ catalyst. A crucial kinetic model for this multi-phase reaction, taking into account statistical analysis, has been proposed. A 2-site model was found to be the most suitable, illustrating aromatic hydrogenation (over a Pt site) and ketone hydrogenation (at the Pt/TiO₂ interface). The selected solvent has little effect on the ketone hydrogenation rate constant, however it strongly influences aromatic hydrogenation due to solvent-catalyst interaction. Reaction selectivity was also corresponded to a fitted product adsorption constant parameter. The role of solvents in affecting reactant adsorption and reaction selectivity was shown by the kinetic analysis method.

Characterising the Rheology of Non-Newtonian Fluids using PFG-NMR and Cumulant Analysis

T. W. Blythe, A. J. Sederman, J. Mitchell, E. H. Stitt, A. P. E. York and L. F. Gladden, *J. Magn. Reson.*, 2015, **255**, 122

A new method to rheometry using pulsed field gradient (PFG) NMR which increases the application of MR rheometry to single-axis gradient hardware was proposed by the present authors. In this study the use of flow propagators was difficult due to the introduction of artefacts during Fourier transform which occur when realistic sampling procedures are limited by experimental and hardware constraints and especially when specific spatial and temporal resolution are needed. In this paper, the authors outline a process involving the cumulant analysis of the acquisition data directly, therefore, avoiding the introduction of artefacts and shortening data acquisition times. A model-dependent method was developed taking into account the pipe-flow characterisation of fluids showing non-Newtonian power-law rheology, which includes using an analytic expression illustrating the flow propagator in terms of the flow behaviour index. This process was found to be resilient to the signal-to-noise ratio (SNR). The simulated results were validated by an experimental investigation on shear-thinning aqueous xanthan gum solutions where the rheology could be correctly characterised using a power-law model across the experimental shear rate range of 1–100 s⁻¹. The calculated flow behaviour indices were found to be within 8% of those acquired using spatially-resolved velocity imaging and within 5% of conventional rheometry.