

Johnson Matthey Highlights

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

EMISSION CONTROL TECHNOLOGIES

[A Comparative Study of N₂O Formation During the Selective Catalytic Reduction of NO_x with NH₃ on Zeolite Supported Cu Catalysts](#)

H.-Y. Chen, Z. Wei, M. Kollar, F. Gao, Y. Wang, J. Szanyi and C. H. F. Peden, *J. Catal.*, 2015, **329**, 490

The decreased N₂O formation on the small pore zeolite, Cu-CHA, in the SCR of NO_x with NH₃ was studied by comparing with a large pore Cu-BEA zeolite catalyst. The N₂O yield rises with a rise in the NO₂/NO_x ratios of the feed gas for both catalysts, implying N₂O is formed *via* the decomposition of NH₄NO₃. TPD showed that NH₄NO₃ was more stable on Cu-CHA compared to Cu-BEA. Surface nitrate groups are vital for NH₄NO₃ formation and this was confirmed by *in situ* FTIR spectra on the stepwise (NO₂ + O₂) and (¹⁵NO + NH₃ + O₂) adsorption and reaction, and product distribution analysis using isotope-labelled reactants. Cu-CHA was found to be significantly less active than Cu-BEA in catalysing NO oxidation and the later formation of surface nitrate groups.

[Local Organization of Fe³⁺ into Nano-CeO₂ with Controlled Morphologies and its Impact on Reducibility Properties](#)

I. Moog, C. Feral-Martin, M. Duttine, A. Wattiaux, C. Prestipino, S. Figueroa, J. Majimel and A. Demourgues, *J. Mater. Chem. A*, 2014, **2**, (47), 20402

Ce_{1-x}Fe_xO_{2-x/2} solid solutions were prepared by two different methods. Surface area, lattice parameter, particle shape and local Fe³⁺ organisation were found to depend on the preparation method and the Fe content. A microwave preparation method was used and caused a large amount of Fe³⁺ to exist in isolated distorted octahedral sites affecting a large number of Ce⁴⁺ nearest neighbours and leading to highly mobile oxygen vacancies. Therefore these samples had a lower solubility limit and a larger variation of the cell parameter compared to conventionally prepared samples. The findings can be extended to provide understanding of reactivity and redox properties (for automotive exhaust catalysts and photocatalysis), ionic conductivity (for

solid oxide fuel cells) and magnetic interactions (for spintronic applications) in other transition metals.

[Thermochemical Recovery Technology for Improved Modern Engine Fuel Economy – Part 1: Analysis of a Prototype Exhaust Gas Fuel Reformer](#)

D. Fennell, J. Herreros, A. Tsolakis, K. Cockle, J. Pignon and P. Millington, *RSC Adv.*, 2015, **5**, (44), 35252

In this study exhaust energy is captured from a high temperature engine exhaust stream to aid catalytic endothermic fuel reforming reactions where hydrocarbon fuel is converted to hydrogen-rich reformat. The reformat is then reused in the engine, providing a source of hydrogen to improve the engine combustion process – known as the reformed exhaust gas recirculation (REGR). This method has much potential for modern gasoline direct injection (GDI) engines. A full scale gasoline prototype reformer incorporated with a multi-cylinder GDI engine was presented by the authors. The prototype reformer performance was analysed by the reformat composition, the temperature distribution across the catalyst, the reforming process efficiency and the amount of exhaust heat recovery accomplished.

FINE CHEMICALS: API MANUFACTURING

[Palladium-Catalyzed \$\alpha\$ -Arylation Reactions in Total Synthesis](#)

S. T. Sivanandan, A. Shaji, I. Ibnusaud, C. C. C. Johansson Seechurn and T. J. Colacot, *Eur. J. Org. Chem.*, 2015, (1), 38

Palladium-catalysed α -arylation of carbonyl compounds is a powerful new methodology for synthesising natural products and active pharmaceutical ingredients (APIs). Increased yields, improved scope, decreased number of steps and alternative starting materials are all made possible. This microreview highlights the importance of the method for a number of challenging examples, and raises to the attention of synthetic chemists the value of palladium-catalysed α -arylation as a key step in choosing a route to structurally important molecules.

NEW BUSINESSES: BATTERY TECHNOLOGIES

Synthesis of Multimodal Porous ZnCo₂O₄ and its Electrochemical Properties as an Anode Material for Lithium Ion Batteries

S. Hao, B. Zhang, S. Ball, M. Copley, Z. Xu, M. Srinivasan, K. Zhou, S. Mhaisalkar and Y. Huang, *J. Power Sources*, 2015, **294**, 112

A simple method to synthesise multimodal porous ZnCo₂O₄ microspheres through PVP assist solvothermal self-assembling process was proposed by the authors. This was then characterised by XRD, SEM, TEM and XPS, and a potential formation mechanism was suggested. Lithium ion batteries were fabricated using the ZnCo₂O₂ microspheres as an anode material. The results show that the porous microstructure gives an outstanding electrochemical performance with high capacity and long-life cycling stability. A large reversible capacity of 940 and 919 mAh g⁻¹ was retained after 100 cycles at a low charge-discharge rate of 0.1 C and 0.2 C (100 and 200 mA g⁻¹) respectively.

NEW BUSINESSES: FUEL CELLS

Platinum/Carbide Interactions: Core-Shells for Catalytic Use

J. L. R. Yates, G. H. Spikes and G. Jones, *Phys. Chem. Chem. Phys.*, 2015, **17**, (6), 4250

Various transition metal carbides were studied by DFT for possible application as core materials in core-shell nanoparticulate fuel cell catalysts. The fcc forms of TiC, NbC, TaC and hcp WC were selected and compared to β SiC. The interaction of model surfaces with Pt were calculated. Pt overlayers on carbides were found to be thermodynamically feasible. The results were explained in terms of the modulation of the carbide and Pt electronic structures. WC and SiC were found to support Pt overlayers and therefore may be suitable for Pt encapsulation. Pt adsorption took place on fcc (111) carbide surfaces in all cases, but not on fcc (100). The carbide supports also affected oxygen binding on the Pt overlayer, the implications for the ORR are discussed. WC may be most suitable for a core material. Several of the Pt-WC surfaces showed reduced oxygen adsorption energies, and should provide similar ORR activity to Pt catalysts.

PRECIOUS METAL PRODUCTS: NOBLE METALS

TEM Characterization of Simultaneous Triple Ion Implanted ODS Fe12Cr

V. de Castro, M. Briceno, S. Lozano-Perez, P. Trocellier, S. G. Roberts and R. Pareja, *J. Nucl. Mater.*, 2014, **455**, (1–3), 157

To aid the design of advanced fusion reactors it is important to understand the behaviour of oxide dispersion strengthened (ODS) ferritic/martensitic

steels under irradiation. TEM was used to investigate the effects of irradiation on a simultaneous triple ion implanted ODS Fe12Cr steel. The grain and dislocation structures, oxide nanoparticles and other secondary phases present in the steel were the focus of the study. Irradiation of the ODS steel was carried out at room temperature using Fe⁸⁺, He⁺ and H⁺ at the JANNUS-Saclay facility to a damage of 4.4 dpa. The ODS nanoparticles had high stability under these irradiation conditions.

PROCESS TECHNOLOGIES

The Adsorption of Ethene on Fe(1 1 1) and Surface Carbide Formation

S. Booyens, L. Gilbert, D. Willock and M. Bowker, *Catal. Today*, 2015, **244**, 122

During Fischer-Tropsch synthesis of higher hydrocarbons from synthesis gas (CO + H₂), ethylene is adsorbed and decomposed on a Fe(1 1 1) surface. This investigation into the nature of the process used a molecular beam reactor and XPS. At a range of substrate temperatures (373–873 K), ethylene was found to decompose fully to atomic carbon and gas phase hydrogen, and carbon deposited on the surface was found to undergo fast diffusion into the subsurface region leaving surface sites free. Fast carbon removal could be achieved with oxygen above ~600 K; the carbon was evolved as CO, with no evidence of CO₂ production. CO on the surface at those temperatures has a very short lifetime.

Dual Doping Effects (Site Blockage and Electronic Promotion) Imposed by Adatoms on Pd Nanocrystals for Catalytic Hydrogen Production

S. Jones, S. M. Fairclough, M. Gordon-Brown, W. Zheng, A. Kolpin, B. Pang, W. C. H. Kuo, J. M. Smith and S. C. E. Tsang, *Chem. Commun.*, 2015, **51**, (1), 46

Doping of metal nanoparticles with additives such as polymers or metallic adatoms can be used to optimise the electronic and geometric properties of catalytic materials. Rational nanocatalyst design can be improved by a greater understanding of doping effects at the atomic level interaction(s). Using the decomposition of HCOOH to H₂/CO₂ over metallic Pd nanoparticles as a probe reaction, three different metal additives were studied: Bi, Te and Ag. Each was found to produce a different doping effect. Bi atoms reside on higher index sites, leading to reduced HCOOH dehydration; Te atoms occupy terrace sites, reducing the rate of dehydrogenation; Ag atoms are not site specific and at high coverage, their strong electronic effects promote activity on the decreased number of surface Pd sites.

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

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

The impact of size reduction mechanisms on γ -Al₂O₃ catalyst support brought about by various stress modes was investigated. Three different mill types were studied and air jet milling was found to be most efficient in decreasing particle size from d_{90} of 37 μm to 2.9 μm in comparison with planetary ball milling (30.2 μm) and single ball milling (10.5 μm). The samples were characterised by XRD and TEM. Phase transformation to the undesirable α -Al₂O₃ occurs during planetary ball milling, therefore, there is a big decrease in the surface area from 136.6 $\text{m}^2 \text{g}^{-1}$ to 82.5 $\text{m}^2 \text{g}^{-1}$ as shown by the BET method. This was caused by the large shear stresses under high shear rates.

Discrete Element Modelling (DEM) Input Parameters: Understanding their Impact on Model Predictions Using Statistical Analysis

Z. Yan, S. K. Wilkinson, E. H. Stitt and M. Marigo, *Comp. Part. Mech.*, 2015, 2, (3), 283

In the DEM, the choice of the particle property input parameters and/or their cross-correlation presents a difficulty. The authors study the effect of the DEM input particle properties on the bulk responses for the discharge of particles from a flat bottom cylindrical container onto a plate using a parametric multi-level sensitivity process. Particle properties such as Young's modulus, friction parameters and coefficient of restitution were altered to investigate the impact on material repose angles and particle flow rate. Both the final angle of repose and particle flow rate are determined by inter-particle static friction followed by inter-particle rolling friction coefficient. The suggested process gives a systematic method that can be used to demonstrate the significance of particular DEM input parameters for a chosen system and then possibly aid their selection or calibration.

Understanding the Structure Directing Action of Copper-polyamine Complexes in the Direct Synthesis of Cu-SAPO-34 and Cu-SAPO-18 Catalysts for the Selective Catalytic Reduction of NO with NH₃

A. Turrina, E. C. V. Eschenroeder, B. E. Bode, J. E. Collier, D. C. Apperley, P. A. Cox, J. L. Casci and P. A. Wright, *Microporous Mesoporous Mater.*, 2015, 215, 154

The direct synthesis of Cu-containing microporous SAPO materials using complexed Cu²⁺ cations in linear polyamines was investigated. The authors studied the complexing ligands: DETA, HEEDA, TETA, 232, 323, TEPA and PEHA. A comparative exercise of the syntheses was undertaken using analogous Ni-polyamine complexes. Both SAPO-18 and SAPO-34 materials were prepared using Cu²⁺ and Ni²⁺. SAPO-18 was prepared with Cu²⁺ (232), Ni²⁺ (232) and Ni²⁺ (TETA) but the majority of the polyamine complexes were prepared by direct crystallisation to SAPO-34. UV-visible, EPR spectroscopy and computer simulation were used to investigate the coordination geometry of the complexes. SAPO-18 was preferred by the smaller square planar complexes or octahedral species (with two water molecules) of 232 and TETA. The extra-framework Cu²⁺ and Ni²⁺ cations in SAPO-18 and SAPO-34 frameworks were caused by calcination. Thermal template degradation happens *via* nitrile intermediates in Ni-SAPO-18 and was shown by *in situ* synchrotron IR spectroscopy. The extra-framework Cu²⁺ and Ni²⁺ cations freed by calcination were located by Rietveld structural analysis.