

Johnson Matthey Highlights

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

EMISSION CONTROL TECHNOLOGIES

'Solid State Platinum Speciation from X-ray Absorption Spectroscopic Studies of Fresh and Road Aged Three Way and Diesel Vehicle Emission Control Catalysts'

T. I. Hyde and G. Sankar, in "Platinum Metals in the Environment", eds. F. Zereini and C. L. S. Wiseman, Environmental Science and Engineering, Springer-Verlag Berlin, Heidelberg, Germany, 2015, pp. 289–308, ISBN: 978-3-662-44558-7 (Print); 978-3-662-44559-4 (Online)

A series of studies were carried out in a variety of locations in Europe and North America on fresh and road-aged automotive catalysts. Platinum L3 and L2 edge X-ray absorption spectroscopy (XAS) was used alongside detailed laboratory based characterisation. X-ray absorption near edge structure (XANES) was found not sufficient to determine the nature of Pt species present in multi-component catalysts. Therefore detailed analysis of the extended X-ray absorption fine structure (EXAFS) was performed at the Pt L3 and L2 edges and this revealed mainly oxidic species to be present in the fresh catalysts, while metallic and bimetallic components were the dominant species in the road aged catalysts. Taken together, with the addition of Cl K-edge XANES analysis, it is concluded that no environmentally significant quantities of chloroplatinate species were present in the fresh or road-aged samples.

'Cu/Zeolite SCR Catalysts for Automotive Diesel NOx Emission Control'

H.-Y. Chen, in "Urea-SCR Technology for deNOx After Treatment of Diesel Exhausts", eds. I. Nova and E. Tronconi, Fundamental and Applied Catalysis, Springer, New York, USA, 2014, pp. 123–147, ISBN: 978-1-4899-8070-0 (Print); 978-1-4899-8071-7 (Online)

The use of Cu/zeolite catalysts for the selective catalytic reduction (SCR) of NO_x with NH₃ is reviewed. Cu/zeolite SCR catalysts exhibit higher NO_x conversion efficiency than titania supported vanadia SCR catalysts, and are also more tolerant to high temperature excursions. This is crucial for automotive applications, in which temperatures above

650°C must be applied periodically to regenerate the diesel particulate filter (DPF). At lower temperatures (200°C–300°C), Cu/zeolite catalysts are more active than alternative Fe/zeolite SCR catalysts. The chemistry and functionality of this class of catalyst is discussed in this book chapter, along with the deactivation mechanisms of previous generations of Cu/zeolite catalysts, the development of small-pore zeolite supported Cu SCR catalysts and recent literature studies on the understanding of their hydrothermal stability and performance.

FINE CHEMICALS: CATALYSIS AND CHIRAL TECHNOLOGIES

Halotriazolium Axle Functionalised [2]Rotaxanes for Anion Recognition: Investigating the Effects of Halogen-Bond Donor and Preorganisation

J. M. Mercurio, R. C. Knighton, J. Cookson and P. D. Beer, *Chem. Eur. J.*, 2014, **20**, (37), 11740

Three novel halogen-bonding 5-halo-1,2,3-triazolium axle containing [2]rotaxanes were prepared by anion-templated synthesis. Different halogen-bond donor atoms and the degree of inter-component preorganisation affected the anion-recognition properties of the interlocked host. This knowledge is vital for designing a potent anion receptor. Bromide was found to be the most effective template from the investigation into the ability of bromotriazolium motif to direct the halide-anion templated assembly of interpenetrated [2]pseudorotaxanes. The first bromotriazolium axle containing [2]rotaxane was synthesised by bromine anion templation and the anion-binding properties were analysed by ¹H NMR spectroscopic titration. The results showed an enhanced bromide and iodide recognition relative to a hydrogen-bonding protic triazolium rotaxane analogue. Two halogen-bonding [2]rotaxanes with bromo- and iodotriazolium motifs arranged into shortened axles designed to extend inter-component preorganisation were also prepared and the rotaxanes were able to bind halide anions even more strongly with the iodotriazolium axle integrated rotaxane capable of recognising halides in aqueous solvent media.

Synthesis and Catalytic Applications of an Extended Range of Tethered Ruthenium(II) η^6 -Arene/Diamine Complexes

R. Hodgkinson, V. Jurčík, A. Zanotti-Gerosa, H. G. Nedden, A. Blackaby, G. J. Clarkson and M. Wills, *Organometallics*, 2014, **33**, (19), 5517

Novel enantiopure Ru(II) complexes were prepared by introducing a tethering group between the η^6 -arene and chiral diamine. An increase in stability and activity at lower catalyst loadings was shown by the complexes and was tested in the asymmetric reduction of various ketones. The presence of bulky sulfonyl groups can influence the reactivity and enantioselectivity of the catalysts.

The Influence of the Hubbard U Parameter in Simulating the Catalytic Behaviour of Cerium Oxide

L. J. Bennett and G. Jones, *Phys. Chem. Chem. Phys.*, 2014, **16**, (39), 21032

The localisation of f -electrons and the self-interaction error linked with DFT can affect the theoretical treatment of ceria. These errors are commonly corrected by DFT + U when investigating specific physical material properties. However, rectifying certain bulk properties may not lead to the correct description of catalytic reactivity at surfaces due to the empirical nature of the U correction. A new method for choosing the U parameter using adsorption properties was proposed in this study. The combination of derived ceria energetics with those of adsorption at metal surfaces enables the construction of transition metal-oxide pairings and a redox screening model for catalysis can be developed.

NEW BUSINESS DEVELOPMENT

Water-Splitting Electrocatalysis in Acid Conditions Using Ruthenate-Iridate Pyrochlores

K. Sardar, E. Petrucco, C. I. Hiley, J. D. B. Sharman, P. P. Wells, A. E. Russell, R. J. Kashtiban, J. Sloan and R. I. Walton, *Angew. Chem. Int. Ed.*, 2014, **53**, (41), 10960

Hydrothermal synthesis was used to prepare for the first time a series of conducting mixed ruthenium–iridium $A_2B_2O_7$ pyrochlore materials with $A = Na, Ce(IV)$ and $B = Ru(IV), Ir(IV)$ as nanocrystalline powders. A solid solution of pyrochlore was used as a catalyst layer for the electrochemical evolution of oxygen from water at pH < 7. The new composition produces electrode coatings with better charge densities than a typical (Ru,Ir) O_2 catalyst. The catalyst was studied *in situ* using XANES. There was no evidence for Ru or Ir in oxidation states +6 or higher. Both Ru and Ir were shown to contribute to the electrocatalytic activity.

NEW BUSINESSES: FUEL CELLS

The Role of the $sp^2:sp^3$ Substrate Content in Carbon Supported Nanotube Growth

R. J. Cartwright, S. Esconjauregui, R. S. Weatherup, D.

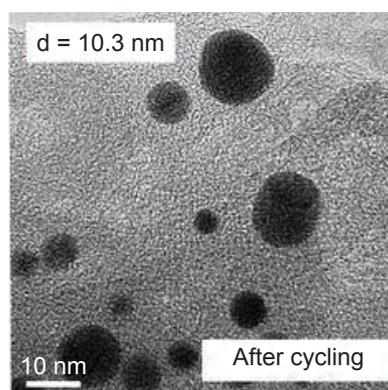
Hardeman, Y. Guo, E. Wright, D. Oakes, S. Hofmann and J. Robertson, *Carbon*, 2014, **75**, 327

Direct growth is the most promising method for incorporating carbon nanotubes (CNTs) into a composite matrix to take advantage of their high tensile strength and surface area to volume ratio for use as nanoscale reinforcement in hierarchical carbon fibre–CNT composites and fuel cell electrodes. In this study, CNTs were grown into ‘forests’ up to 0.2 mm high on an 85:15 $sp^2:sp^3$ carbon support with Fe catalyst. The catalyst was pretreated in inert atmosphere to avoid the growth of defective CNTs. Graphite, tetrahedral amorphous carbon and pure diamond were also found to produce defective CNTs. The importance of the substrate in controlling the growth of CNTs on carbon fibres has been emphasised.

Degradation Mechanisms of Platinum Nanoparticle Catalysts in Proton Exchange Membrane Fuel Cells: The Role of Particle Size

K. Yu, D. J. Groom, X. Wang, Z. Yang, M. Gummalla, S. C. Ball, D. J. Myers and P. J. Ferreira, *Chem. Mater.*, 2014, **26**, (19), 5540

Morphological changes in the Pt nanoparticle catalysts during fuel cell operation, particularly in the cathode, are associated with performance degradation. This article presents the first systematic study by transmission electron microscopy (TEM) analysis of the influence of nanoparticle size on active degradation mechanisms and hence on the electrochemical performance of membrane electrode assemblies (MEAs). Five MEAs with different average sizes of Pt nanoparticles in the cathode were analysed before and after potential cycling (see **Figure**). In most cases, the smallest initial particle size catalysts ended up with the largest particle sizes after 10,000 cycles, meaning that the ECA loss for Pt nanoparticle catalysts with smaller initial sizes (2.2 nm and 3.5 nm) was greater than for particles with sizes from 5.0 nm to 11.3 nm. Mechanisms for the particle size changes are discussed.



Reprinted with permission from K. Yu, D. J. Groom, X. Wang, Z. Yang, M. Gummalla, S. C. Ball, D. J. Myers and P. J. Ferreira, *Chem. Mater.*, 2014, **26**, (19), 5540. Copyright (2014) American Chemical Society

Record Activity and Stability of Dealloyed Bimetallic Catalysts for Proton Exchange Membrane Fuel Cells

B. Han, C. E. Carlton, A. Kongkanand, R. S. Kukreja, B. R. Theobald, L. Gan, R. O'Malley, P. Strasser, F. T. Wagner and Y. Shao-Horn, *Energy Environ. Sci.*, 2015, doi:10.1039/C4EE02144D

The highest catalyst activity and device durability yet achieved in PEMFCs under automotive testing conditions is reported. A family of dealloyed core-shell Pt-Ni nanoparticles were developed as catalysts for the cathode. Smaller particle size, non-oxidative acid treatment and post-acid-treatment annealing was found to reduce transition metal leaching from catalyst nanoparticles, and suppress nanoporosity formation. This insight led to the ability to design more stable and active Pt-Ni catalysts. The details of alloy structure and compositions that lead to long-term PEMFC device stability were analysed using SEM and EDS. The resulting catalyst meets and exceeds the official 2017 DOE targets for the oxygen reduction reaction (ORR).

PROCESS TECHNOLOGIES

FCC Additive Improves Residue Processing Economics with High Iron Feeds

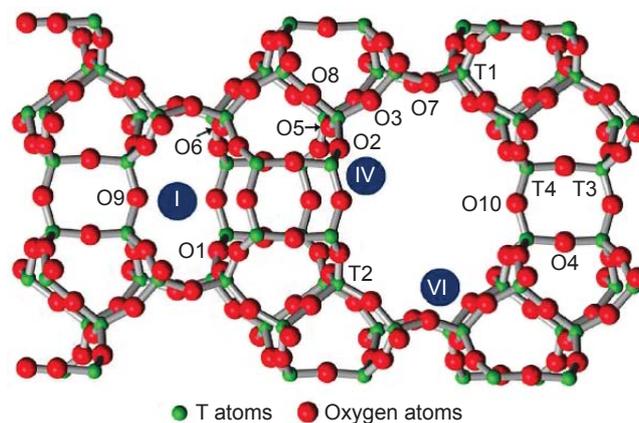
T. Hochheiser, Y. Tang, M. Allahverdi and B. De Graaf, American Fuel and Petrochemical Manufacturers (AFPM) Annual Meeting, Orlando, USA, 23rd–25th March, 2014

Johnson Matthey's FCC INTERCAT_{JM} additive CAT-AIDTM is used by many refineries to trap contaminants due to its ability to improve the profitability of the FCC operation. Lower quantities of fresh catalyst and flushing Ecat are needed and the product selectivities are improved, in particular diminishing delta coke. This study includes three commercial examples and the use of CAT-AIDTM to reduce delta coke and improve residue processing is demonstrated.

Insights into Brønsted Acid Sites in the Zeolite Mordenite

D. B. Lukyanov, T. Vazhnova, N. Cherkasov, J. L. Casci and J. J. Birtill, *J. Phys. Chem. C*, 2014, 118, (41), 23918

The purpose of this study was to identify the exact number and locations of Brønsted acid sites (BAS) in acidic and partially Na-exchanged samples of zeolite mordenite (MOR). The catalytic properties of MOR are notably influenced by the local environment of the BAS (O1–O10 atoms), see **Figure**. At least six distinct BAS in the MOR structure were identified by a comprehensive FT-IR investigation and Fourier self-deconvolution (FSD) analysis of the IR spectra. The results showed that ~25% of BAS are located in the eight-membered ring (8-MR) channels (O1–H and O9–H) in the purely acidic H-MOR sample, ~13% of BAS are found at the intersections between the side pockets and 12-MR channels (O5–H hydroxyls) and ~62% of BAS are located in 12-MR channels (~39% correlate to O2–H and/or O10–H hydroxyls and the remaining 23% to O3–H and O7–H hydroxyls). The acid sites were found to be distributed quite evenly between oxygen atoms in the various crystallographic positions.



Reprinted with permission from D. B. Lukyanov, T. Vazhnova, N. Cherkasov, J. L. Casci and J. J. Birtill, *J. Phys. Chem. C*, 2014, 118, (41), 23918. Copyright (2014) American Chemical Society