

Johnson Matthey Highlights

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

EMISSION CONTROL TECHNOLOGIES

Increased NO₂ Concentration in the Diesel Engine Exhaust for Improved Ag/Al₂O₃ Catalyst NH₃-SCR Activity

W. Wang, J. M. Herreros, A. Tsolakis and A. P. E. York, *Chem. Eng. J.*, 2015, **270**, 582

Fast-SCR was investigated for NO_x reduction in internal combustion engines. H₂ addition was found to increase NO₂ formation over a Ag/Al₂O₃ catalyst. This led to an improved NH₃-SCR activity at low temperature. It is concluded that NO₂ formation before the Ag/Al₂O₃ catalyst either in the engine or a Pt/Al₂O₃ based DOC will improve SCR performance. This NO₂ promotion effect was less at higher temperatures.

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

Reformed exhaust gas recirculation (REGR) provides H₂ to the combustion process to recover heat from exhaust and improve fuel conversion efficiency. A full scale prototype reformer for gasoline direct injection engines is presented and its performance is assessed. The performance is better at higher temperatures with a decline in performance at lower exhaust temperature. The reformate quality is also dependent on process temperature and reactant composition.

FINE CHEMICALS

Palladium-Catalyzed α -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

New methods for synthesising natural products and active pharmaceutical ingredients have been explored using palladium-catalysed α -arylation of carbonyl compounds. The advantages of this particular method are an increase in the overall yield, an improved synthesis scope and a reduction in the number of steps.

The significance of palladium-catalysed α -arylation methods are discussed and a number of case studies have been included.

The Effects of 1-pentyne Hydrogenation on the Atomic Structures of Size-selected Au_N and Pd_N (N = 923 and 2057) Nanoclusters

K.-J. Hu, S. R. Plant, P. R. Ellis, C. M. Brown, P. T. Bishop and R. E. Palmer, *Phys. Chem. Chem. Phys.*, 2014, **16**, (48), 26631

The variation in atomic structures of size-selected Au and Pd nanoclusters (containing 923 and 2057 atoms) supported on amorphous carbon films before and after being exposed to the vapour-phase hydrogenation of 1-pentyne was studied. The populations of the nanoclusters were studied at atomic resolution before and after the reaction using an aberration-corrected high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM). The atomic structures of the observed nanoclusters were determined by comparing the multi-slice HAADF-STEM and experimental images for a full range of cluster orientations. The results show that Au nanoclusters consisting of 923 \pm 20 and 2057 \pm 45 atoms are robust and exhibit high structural stability. A big proportion of Pd_{923 \pm 26} nanoclusters, on the other hand, appear to be amorphous before the treatment and after the reaction were found to exhibit high symmetry structures which suggests the reduction of oxidised Pd nanoclusters in reaction conditions.

FINE CHEMICALS: CATALYSIS AND CHIRAL TECHNOLOGIES

Stereoselective Synthesis of the Halaven C14-C26 Fragment from D-Quinic Acid: Crystallization-Induced Diastereoselective Transformation of an α -Methyl Nitrile

F. Belanger, C. E. Chase, A. Endo, F. G. Fang, J. Li, S. R. Mathieu, A. Z. Wilcoxon and H. Zhang, *Angew. Chem. Int. Ed.*, 2015, **54**, (17), 5108

A series of substrate controlled stereoselective reactions with crystalline intermediates was carried out *via* an α -methyl nitrile to produce a C14–C26 fragment of halichondrin B/Halaven. The synthesis does not require

chromatography and relies entirely on crystallisation for quality control. D-quinic acid is the starting material, providing all four chiral centres, and is readily available. Raw material cost and waste are both reduced by the present synthesis.

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

Halogen bonding has been little explored outside the areas of solid state crystal engineering. A novel halogen bonding rotaxane structure was prepared for use in anion recognition and exhibits good anion recognition and sensing properties. An ion templated Grubbs' II-catalysed RCM clipping mechanical bond forming was used to synthesise the structure which contains both halogen- and hydrogen-bonding macrocyclic components. ^1H NMR spectroscopy and fluorescence titration experiments were carried out and showed that the new structure can strongly associate with acetate and dihydrogen phosphate.

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

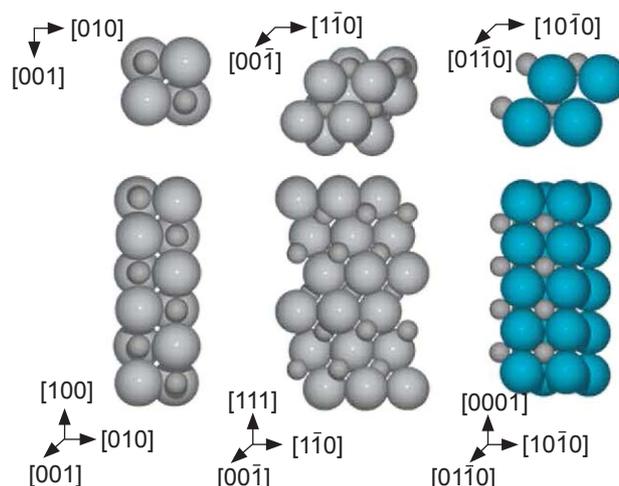
Five carbides (TiC, NbC, TaC, WC and SiC) were investigated using density functional theory with the aim of determining their suitability as core-shell components in fuel cell applications. The fcc forms of the carbides were compared with hexagonal close-packed (hcp) WC and zinc blende SiC and the latter was found to support Pt overlayers on surfaces, therefore, showing potential for full Pt encapsulation. The transition metal surface resonances (TMSRs) play a vital role during the adsorption of Pt on fcc (111) carbide surfaces and fcc (100) was found to be adverse towards Pt adsorption. Reduced oxygen adsorption energies was displayed by several Pt-WC surfaces during the oxygen adsorption study; the authors conclude that ORR activity should be promoted or maintained with respect to nanoparticulate Pt catalysts.

PROCESS TECHNOLOGIES

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

Additives based on polymer or metal adatoms can modify the electronic structure of metal nanoparticles but greater understanding of atomic level effects



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is needed to rationally design better catalysts by surface tailoring. Electronic and geometric effects of various metals on unsupported Pd nanocrystals were investigated using the decomposition of HCOOH to H_2 and CO_2 as a probe reaction. Bi was found to occupy high index sites causing a decrease in HCOOH dehydration, Te occupies terrace sites which reduces the dehydrogenation rate while Ag induced strong electronic effects and increased the activity of the Pd surface sites. Ag and Bi were concluded to be the most effective additives for a surface reaction, while Te should be added at corner sites to promote the desired reaction route.

Surfactant Mediated CO_2 Adsorption: The Role of the Coimpregnation Species

C. M. Starkie, A. Amieiro-Fonseca, S. P. Rigby, T. C. Drage and E. H. Lester, *Energy Procedia*, 2014, **63**, 2323

Carbon capture and storage requires novel, second generation adsorbent systems to potentially reduce costs associated with this technology. Solid supported amines have been investigated. These consist of basic amines either tethered or impregnated on silica or alumina and co-impregnated with surfactant additives. The mechanisms of adsorption of these systems were studied and they were shown to have 55% improved working capacity relative to single component systems. Triethanolamine and sodium dodecylsulfate produced the best adsorbent properties.

The Synergistic Effect in the Fe-Co Bimetallic Catalyst System for the Growth of Carbon Nanotube Forests

D. Hardeman, S. Esconjauregui, R. Cartwright, S. Bhardwaj, L. D'Arzié, D. Oakes, J. Clark, C. Cepek, C. Ducati and J. Robertson, *J. Appl. Phys.*, 2015, **117**, (4), 044308

The growth of multi-walled carbon nanotube forests using an active bimetallic Fe-Co catalyst was investigated. When this bimetallic catalyst system was compared to pure Fe or Co a synergistic effect is observed. The height of the forests was considerably increased and an improvement of the homogeneity in the as-grown nanotubes was found. The catalyst system was characterised using energy dispersive spectroscopy and *in situ* X-ray photoelectron spectroscopy. The authors conclude that the growth rate of the nanotubes is greatly improved in the presence of Fe and Co.

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

The performance of oxide dispersion strengthened (ODS) ferritic/martensitic steels under irradiation is studied. This is essential in the design of advanced fusion reactors. Transmission electron microscopy was used to characterise a simultaneous triple ion implanted ODS Fe12Cr steel with the aim of investigating the impact of irradiation on the grain and dislocation structures, oxide nanoparticles and other secondary phases present in

steel. The ODS steel was irradiated simultaneously with Fe⁸⁺, He⁺ and H⁺ at room temperature to a damage of 4.4 dpa at the Joint Accelerators for Nanosciences and Nuclear Simulation (JANNUS) Saclay facility. The authors concluded that ODS nanoparticles are very stable under these irradiation conditions.

An Experimental Investigation of Biodiesel Steam Reforming

S. Martin, G. Kraaij, T. Ascher, D. Wails and A. Wörner, *Intl. J. Hydrogen Energy*, 2015, **40**, (1), 95

The optimum operating conditions of a proprietary precious metal based catalyst for biodiesel steam reforming was investigated with the aim of preventing catalyst deactivation. Different operating conditions include varying the temperature from 600°C to 800°C, applying different pressure from 1 bar to 5 bar and altering the molar steam-to-carbon ratio from 3 to 5. Coke formation and sintering have been determined as the main deactivation mechanisms. The authors conclude that coking can be reduced by using low feed flow rates (31 g h⁻¹ cm⁻²) and a relatively high catalyst inlet temperature (>750°C).