JOHNSON MATTHEY
TECHNOLOGY REVIEW

www.technology.matthey.com

Johnson Matthey Highlights

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

EMISSION CONTROL TECHNOLOGIES

Kinetic Evaluation of Direct NO Decomposition and NO-CO Reaction over Dendrimer-derived Bimetallic Ir-Au/Al$_2$O$_3$ Catalysts

Y.-J. Song, Y. M. López-De Jesús, P. T. Fanson and C. T. Williams, *Appl. Catal. B: Environ.*, 2014, **154–155**, 62

The performance of a dendrimer-derived bimetallic Au-Ir catalyst for the reduction of NO by CO and also for direct NO decomposition were studied and compared to a more conventional bimetallic catalyst, prepared using incipient wetness impregnation. Analysis of the dendrimer-derived catalyst showed highly dispersed Ir-Au particles and it exhibited better catalytic performance for both reactions when compared to the conventional catalyst. A structural effect due to Au was noted for the conventional catalyst which was not seen for the dendrimer-derived catalyst due to the fact the Au was so highly dispersed. On the conventional catalyst, Au particles appear to dilute the surface Ir sites, resulting in higher TOF when compared to monometallic Ir catalysts prepared using the same incipient wetness technique.

Prediction of Diffusivity and Conversion of *n*-Decane and CO in Coated Pt/γ-Al$_2$O$_3$ Catalyst Depending on Porous Layer Morphology

M. Dudák, V. Novák, P. Kočí, M. Marek, P. Blanco-García and G. Jones, *Appl. Catal. B: Environ.*, 2014, **150–151**, 446

The effects of diffusion in the catalytic layer, especially if there are multiple coated layers, can limit the conversion in monolith reactors for automotive exhaust gas aftertreatment. Therefore a good understanding of the internal diffusion effects is required for designing an optimum catalytic coating. A detailed multiscale modelling technique including the use of 3D digital reconstruction is used to predict the effective diffusivity based on the actual structure of a porous coating. A 3D digitally reconstructed porous layer structure enabled the simulation of diffusion and oxidation of CO and *n*-decane on a microscale. The simulations were then compared with experiments which involved the coating of several layers with uniform thickness on flat metal foils and controlling its macroporous structure by changing the alumina particle size distribution, pore templates and compaction methods. The reactor outlet conversions were calculated using a macroscopic 1D plug-flow model. The comparison shows good agreement: the predicted effective diffusion coefficients through the tested Pt/γ-Al$_2$O$_3$ layers were 1.4, 3.6 and 6.4 × 10^{-6} m^2 s^{-1} for CO at 298 K in compact, standard and macropore-templated sample, respectively.
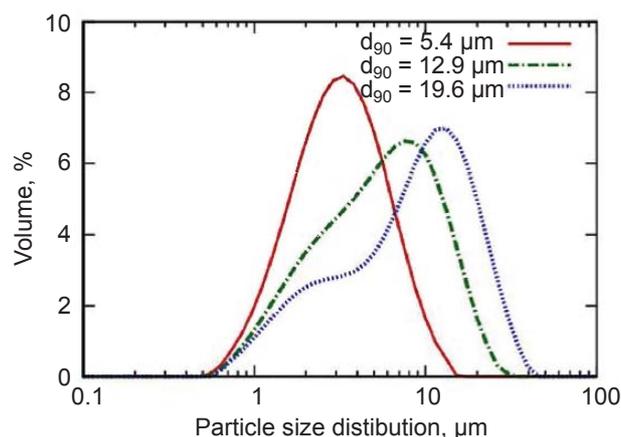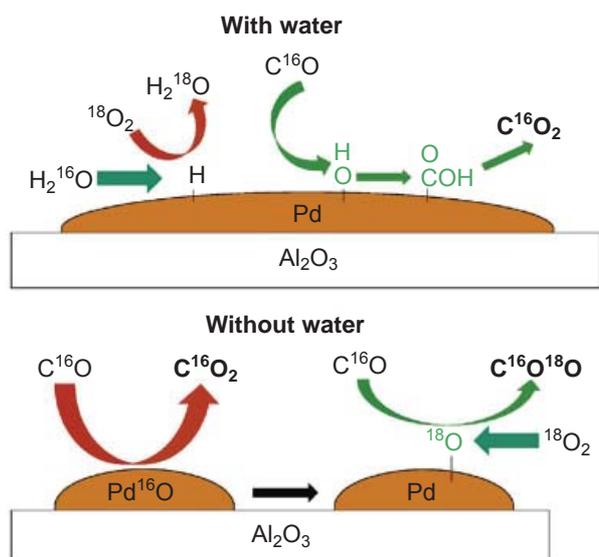

M. Dudák *et al.*, *Appl. Catal. B: Environ.*, 2014, **150–151**, 446

Critical Role of Water in the Direct Oxidation of CO and Hydrocarbons in Diesel Exhaust After Treatment Catalysis

R. Caporali, S. Chansai, R. Burch, J. J. Delgado, A. Goguet, C. Hardacre, L. Mantarosie and D. Thompsett, *Appl. Catal. B: Environ.*, 2014, **147**, 764

The oxidation of CO and C$_3$H$_6$ over a Pd/Al$_2$O$_3$ catalyst were studied using isotopically labelled ^{18}O$_2$. Water was found to promote CO and cause C$_3$H$_6$ to be oxidised at lower temperatures compared to a dry feed. The reaction mechanism was elucidated by adding a labelled ^{18}O$_2$ as the reactant, revealing that the main pathway in the presence of water is *via* water activation, while O$_2$ plays a secondary role. D$_2$O significantly decreased this effect compared to H$_2$O, further supporting the importance of water activation (see **Figure**).

With water

R. Caporali *et al.*, *Appl. Catal. B: Environ.*, 2014, **147**, 764

The Role of Pore Size on the Thermal Stability of Zeolite Supported Cu SCR Catalysts

P. G. Blakeman, E. M. Burkholder, H.-Y. Chen, J. E. Collier, J. M. Fedeyko, H. Jobson and R. R. Rajaram, *Catal. Today*, 2014, **231**, 56

In situ XRD has been used to carry out a comparison study on the effects of pore size on the hydrothermal stability of zeolite supported Cu SCR catalysts. Small pore catalysts were found to be more stable than large or medium pore catalysts. The supports studied were an 8-ring small pore chabazite (CHA) and a 12-ring large pore beta zeolite (BEA). Even though the parent zeolite frameworks have comparable stability and can maintain their structure after hydrothermal exposure at 900ºC, the presence of Cu increased the rate of collapse of the BEA framework above 800ºC while having little effect on the CHA framework. This is thought to be due to a harmful Cu/Al_2O_3 interaction. The steric restriction of the small pore zeolite structure may hinder this interaction allowing the stability to be improved.

Local Structure and Speciation of Platinum in Fresh and Road-Aged North American Sourced Vehicle Emissions Catalysts: An X-Ray Absorption Spectroscopic Study

P. W. Ash, D. A. Boyd, T. I. Hyde, J. L. Keating, G. Randlshofer, K. Rothenbacher, G. Sankar, J. J. Schauer, M. M. Shafer and B. M. Toner, *Environ. Sci. Technol.*, 2014, **48**, (7), 3658

The Pt species present in a range of fresh and road-aged three-way and diesel oxidation catalysts from North America were studied using Pt and Cl XAS in order to identify the Pt compounds that may be released into the environment from such sources. The main species present in the fresh catalyst were found to be oxides. In the road-aged catalysts, the main species were metallic. There were also some bimetallic components such as Pt-Ni, Pt-Pd and Pt-Rh. Significantly, there was no evidence of chloroplatinate species in the solid phase for any of the catalysts studied.

FINE CHEMICALS: CATALYSIS AND CHIRAL TECHNOLOGIES

An Efficient Catalytic Asymmetric Synthesis of a β^2-Amino Acid on Multikilogram Scale

T. Remarchuk, S. Babu, J. Stults, A. Zanotti-Gerosa, S. Roseblade, S. Yang, P. Huang, C. Sha and Y. Wang, *Org. Process. Res. Dev.*, 2014, **18**, (1), 135

Research was carried out to tackle the challenges surrounding a kilogram-scale production of chiral β^2-amino acid derivatives by catalytic asymmetric hydrogenation. The authors developed a short and efficient synthesis of an unsaturated *N*-Boc protected β^2-enamide precursor and chiral catalyst screening was then carried out on common and readily available chiral metal complexes of Rh, Ru and Ir which would generate β^2-amino acid in high enantiomeric excess. Optimisation experiments were then conducted to identify optimum reaction conditions and investigate the effectiveness of additives in terms of improvements in reactivity and enantioselectivity. A simple Ru-BINAP catalyst system was found to generate the (*S*) product in high enantiomeric excess (>99% ee) and yield. Production on a multikilogram scale resulted in >99% ee.

NEW BUSINESSES: FUEL CELLS

The Origin of High Activity But Low CO_2 Selectivity on Binary PtSn in the Direct Ethanol Fuel Cell

J.-M. Jin, T. Sheng, X. Lin, R. Kavanagh, P. Hamer, P. Hu, C. Hardacre, A. Martinez-Bonastre, J. Sharman, D. Thompsett and W.-F. Lin, *Phys. Chem. Chem. Phys.*, 2014, **16**, (20), 9432

DEFCs are an attractive technology as they can use carbon-neutral bioethanol as a fuel. The challenge is to find a more efficient electrocatalyst for the anode, in terms of both activity at low overpotential and CO_2 selectivity. In this study, variable temperature electrochemical *in situ* FTIR was applied to the study of an active binary PtSn DEFC catalyst at 20ºC and at 60ºC. The binary PtSn catalyst was found to be better than Pt at inhibiting EtOH dissociation to CO, but to promote the partial oxidation to acetaldehyde and acetic acid. At 60ºC there was enhanced CO_2 selectivity due to an increase in both EtOH dissociation to CO and further oxidation to CO_2. The main products were still found to be acetaldehyde and acetic acid at 60ºC. Density functional theory (DFT) calculations were used to derive the potential-dependent phase diagrams for surface oxidants of OH formation on Pt(111), Pt(211) and Sn modified Pt(111) and Pt(211) surfaces and the results provide insight into these experimental results at the atomic and molecular levels.

PRECIOUS METAL PRODUCTS: COLOUR TECHNOLOGIES

Aerosol-Assisted Deposition of Gold Nanoparticle-Tin Dioxide Composite Films

C. Chew, P. Bishop, C. Salcianu, C. J. Carmalt and I. P. Parkin, *RSC Adv.*, 2014, **4**, (25), 13182

Aerosol assisted chemical vapour deposition (AACVD) was used to investigate the formation of tin oxide films with embedded gold nanoparticles. The purpose of the study was to find out if gold could be used as a colourant in a CVD derived film. In this study, AACVD involves the growth of composite gold nanoparticle/tin oxide films from a one-pot precursor solution containing monobutyltin trichloride and auric acid in methanol. Two films were formed: gold nanoparticle films on the top plate and gold/tin dioxide composite film on the heated substrate. Depending on the position from the inlet, different amounts of gold incorporation were shown on the composite film thus a graded film was formed, therefore enabling the authors to assess the functional properties of the films. 0.03–0.15 Au:Sn molar ratio was found to be the optimum location where a mix of desirable properties such as blue colouration, reasonable optical transparency as well as reflectivity in the IR were observed.

PROCESS TECHNOLOGIES

Understanding the Optimal Adsorption Energies for Catalyst Screening in Heterogeneous Catalysis

B. Yang, R. Burch, C. Hardacre, G. Headdock and P. Hu, *ACS Catal.*, 2014, **4**, (1), 182

In this research a two-step model was used by the authors to understand the kinetics of heterogeneous catalysts and help to predict which catalysts will perform best. The model provides a simplified description of real-world systems, only modelling those systems with a single rate-determining step. Detailed analysis of volcano curves was carried out, and related to adsorption energies and other terms from the Brønsted−Evans−Polanyi (BEP) relation. The authors derive conditions in terms of the energy window which should allow for optimal catalysts to be designed.

Improving Sensitivity and Accuracy of Pore Structural Characterisation Using Scanning Curves in Integrated Gas Sorption and Mercury Porosimetry Experiments

I. Hitchcock, M. Lunel, S. Bakalis, R. S. Fletcher, E. M. Holt and S. P. Rigby, *J. Colloid Interface Sci.*, 2014, **417**, 88

An integrated gas sorption and mercury porosimetry technique is demonstrated which can detect pores within disordered solids which are undetectable when using conventional scanning experiments. On its own gas sorption was not sensitive enough to detect these pores, but the combined technique proved more powerful than either of the two individual methods on their own. Pore-filling mechanisms were found to vary in disordered solids, and so this integrated technique allows for a more accurate calculation of pore size distribution by avoiding the introduction of systematic errors due to the assumption of a single filling mechanism taking place.

Mechanistic Study of 1,3-Butadiene Formation in Acetylene Hydrogenation Over the Pd-based Catalysts Using Density Functional Calculations

B. Yang, R. Burch, C. Hardacre, P. Hu and P. Hughes, *J. Phys. Chem.*, 2014, **118**, (3), 1560

During the selective hydrogenation of acetylene in commercial processes, one deactivation route for the palladium catalyst is due to the formation of green oil. The mechanisms behind the formation of this catalyst poison are not well known, but the formation of 1,3-butadiene is thought to be a precursor for green oil. This research uses density functional theory to investigate the likely reaction pathways over Pd(111) and Pd (211) surfaces for the formation of 1,3-butadiene in an attempt to understand the mechanisms of green oil formation. A combination of hydrogenation and coupling reactions of C_2 groups is believed to take place and therefore three potential routes to the formation of green oil were modelled resulting in a general explanation for the deactivation process of industrial catalysts. The effect of subsurface carbon atom formation was also studied, as well as that of Ag alloying on the 1,3-butadiene formation using Pd-based catalysts with the results comparing well with experimental results.

Moving from Batch to Continuous Operation for the Liquid Phase Dehydrogenation of Tetrahydrocarbazole

Y. Shen, A. Maamor, J. Abu-Dharieh, J. M. Thompson, B. Kalirai, E. H. Stitt and D. W. Rooney, *Org. Process. Res. Dev.*, 2014, **18**, (3), 392

The liquid phase processing of fine chemicals is usually carried out using batch operation. However, the benefits of continuous operation such as decreased times for start-up and cool-down cycles, improved process safety and more stable reaction conditions should be taken into consideration. In this paper, the authors study the liquid phase dehydrogenation reaction of 1,2,3,4-tetrahydrocarbazole under continuous operation using a trickle bed reactor. The experiments were performed using realistic liquid velocities with and without the presence of a hydrogen acceptor. Under continuous use a commercial 5 wt% Pd/Al_2O_3 catalyst was found to slowly deactivate, however this problem is overcome when the catalyst is washed with sodium hydroxide. It was observed that the use of propene as a hydrogen acceptor gas can increase the overall catalytic activity of the operation.