

## Johnson Matthey Highlights

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

#### Understanding Methanol Synthesis from CO/H<sub>2</sub> Feeds over Cu/CeO<sub>2</sub> Catalysts

L. G. A. van de Water, S. K. Wilkinson, R. A. P. Smith and M. J. Watson, *J. Catal.*, 2018, **364**, 57

Results of a methanol synthesis study over a Cu/CeO<sub>2</sub> catalyst using CO/H<sub>2</sub> feeds are presented, using catalyst characterisation data combined with catalyst performance data. These results indicate that the reaction mechanism and active site for methanol synthesis over Cu/CeO<sub>2</sub> are different from the Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst. CO, instead of CO<sub>2</sub>, is the carbon source for methanol. Stepwise CO hydrogenation is the most likely mechanism for methanol formation. Self-poisoning of the Cu<sup>+</sup>/CeO<sub>2-x</sub> active sites occurs through build-up of carbonate and formate species on the catalyst surface. The level of deactivation can be controlled by changes in CO content in the feed. The key difference between the two systems is the absence of CO<sub>2</sub> and H<sub>2</sub> reabsorption, formed during catalyst activation, on the Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst.

#### Durability of De-Alloyed Platinum-Nickel Cathode Catalyst in Low Platinum Loading Membrane-Electrode Assemblies Subjected to Accelerated Stress Tests

R. K. Ahluwalia, X. Wang, J.-K. Peng, N. N. Kariuki, D. J. Myers, S. Rasouli, P. J. Ferreira, Z. Yang, A. Martinez-Bonastre, D. Fongalland and J. Sharman, *J. Electrochem. Soc.*, 2018, **165**, (6), F3316

The durability of de-alloyed platinum-nickel catalyst supported on high-surface area carbon (d-PtNi/C) in optimised electrodes and membrane electrode assemblies was investigated. These were under an accelerated stress test protocol with the objective of developing a quantitative understanding of the degradation mechanisms. The relationship to the electrode structure, preconditioning and operating conditions were also studied.

#### An Alternative Route to Tethered Ru(II) Transfer Hydrogenation Catalysts

R. Hodgkinson, V. Jurčák, H. Nedden, A. Blackaby and M. Wills, *Tetrahedron Lett.*, 2018, **59**, (10), 930

The route to tethered η<sup>6</sup>-arene/Ru(II) catalysts proceeds through the formation of an amide from the diamine precursor, followed by reduction, rather than the direct alkylation of the diamine. This gives the advantage that dialkylation of the amine is avoided during synthesis. The new route introduces both racemic and enantiomerically-pure η<sup>6</sup>-arene/Ru(II) tethered catalysts in high yield. The clean reductions, without complication of side-product formation, using an economical metal source, provide an advantage over more established stoichiometric methods.

#### High-Resolution Analysis of Ionomer Loss in Catalytic Layers after Operation

T. Morawietz, M. Handl, C. Oldani, P. Gazdzicki, J. Hunger, F. Wilhelm, J. Blake, K. A. Friedrich and R. Hiesgen, *J. Electrochem. Soc.*, 2018, **165**, (6), F3139

The function of catalytic layers in fuel cells and electrolyzers depends on the properties of the ionically conductive phase. An analysis by atomic force microscopy reveals that the ultrathin ionomer films around Pt/C agglomerates have a thickness distribution ranging from 3.5 nm to 20 nm. Their conductivity and gas permeation properties determine the fuel cell performance to a large extent. The observed thinning of the ultrathin ionomer films was mainly caused by polymer degradation deduced from reduced swelling after long-time operation and a significant loss of ionomer with operation time detected by infrared spectroscopy.

### Isotopic Characterization of Mercury in Natural Gas via Analysis of Mercury Removal Unit Catalysts

S. J. Washburn, J. D. Blum, M. W. Johnson, J. M. Tomes and P. J. Carnell, *ACS Earth Space Chem.*, 2018, **2**, (5), 462

The overall amount of mercury (Hg) released to the atmosphere is largely unknown but gaseous elemental Hg release is likely an increasing contribution to the global atmospheric Hg pool. To characterise the isotopic composition of Hg released from natural gas (NG), this paper presents an analysis of the stable isotopic compositions of mercury removal unit (MRU) catalysts that were loaded with Hg from NG production and supplied by Johnson Matthey Inc, USA. It is suggested that the bulk of Hg absorbed to catalysts near the inlet of each MRU reactor is representative of the Hg isotopic composition of Hg in the NG source.

### Deceleration of SO<sub>2</sub> Poisoning on PtPd/Al<sub>2</sub>O<sub>3</sub> Catalyst During Complete Methane Oxidation

N. Sadokhina, G. Smedler, U. Nylén, M. Olofsson and L. Olsson, *Appl. Catal. B: Environ.*, 2018, **236**, 384

*In situ* DRIFT spectroscopy, characterisation with XPS, STEM-EDX and flow reactor experiments were performed. It was found that the addition of Pt to Pd/Al<sub>2</sub>O<sub>3</sub> resulted in a catalyst that was more robust towards sulfur poisoning. XPS results revealed residual sulfates on the catalyst surface after regeneration. Although the catalyst had been deactivated in the presence of both SO<sub>2</sub> and H<sub>2</sub>O, an additional presence of NO in the gas mixture of reactants resulted in an increase in lifetime of the sample under reaction conditions.

### Development of Low Mass-Transfer-Resistance Fluorinated TiO<sub>2</sub>-SiO<sub>2</sub>/PVDF Composite Hollow Fiber Membrane used for Biogas Upgrading in Gas-Liquid Membrane Contactor

Y. Xu, Y. Lin, M. Lee, C. Malde and R. Wang, *J. Membrane Sci.*, 2018, **552**, 253

The authors propose a facile method for preparing an inorganic/organic fluorinated titania-silica (fTiO<sub>2</sub>-SiO<sub>2</sub>)/polyvinylidene fluoride (PVDF) composite hollow fibre membrane, for CO<sub>2</sub> removal in gas-liquid membrane contactor application. An *in situ* vapour-induced hydrolysis method was used. Good integrity between the fTiO<sub>2</sub>-SiO<sub>2</sub> layer and the PVDF substrate was achieved. The fTiO<sub>2</sub>-SiO<sub>2</sub> layer demonstrated strong chemical resistance and high hydrophobicity, with a pore size of ~25 nm, a water contact angle of ~124° and CO<sub>2</sub> absorption fluxes of 8.0 and 5.6 × 10<sup>-3</sup> mol m<sup>-2</sup> s<sup>-1</sup>. These attributes were the result of using monoethanolamine and sodium taurinate as absorbents at 0.25 m s<sup>-1</sup> and controlling Si precursors.

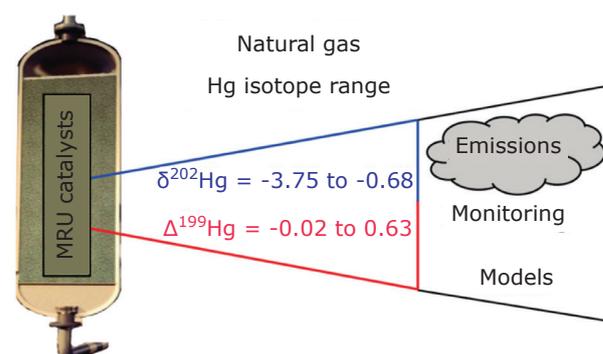


Fig. 1. Reprinted with permission from S. J. Washburn, J. D. Blum, M. W. Johnson, J. M. Tomes and P. J. Carnell, *ACS Earth Space Chem.*, 2018, **2**, (5), 462. Copyright 2018 American Chemical Society.

### Dominant Effect of Support Wettability on the Reaction Pathway for Catalytic Wet Air Oxidation over Pt and Ru Nanoparticle Catalysts

D. Davies, S. Golunski, P. Johnston, G. Lalev and S. H. Taylor, *ACS Catal.*, 2018, **8**, (4), 2730

The role of support wettability in directing the activation of oxygen during catalytic wet air oxidation over nanoparticle catalysts is shown to be of greater importance than the effects of ceria. The optimum support is dependent on the composition of the nanoparticle catalyst. With an ionic Ru catalyst, where O<sub>2</sub> is adsorbed in the aqueous phase, a hydrophilic support is the most effective. In contrast with a metallic Pt catalyst, where gas-phase O<sub>2</sub> is adsorbed directly on the Pt surface, a hydrophobic support is the most advantageous.

### Cyclometalated Dicarboxyl Ruthenium Catalysts for Transfer Hydrogenation and Hydrogenation of Carbonyl Compounds

S. Giboulot, S. Baldino, M. Ballico, H. G. Nedden, D. Zuccaccia and W. Baratta, *Organometallics*, 2018, **37**, (13), 2136

The preparation of five cyclometalated dicarboxyl ruthenium complexes is reported. All five complexes were shown to catalyse the hydrogenation (HY) of several ketones (H<sub>2</sub>, 30 bar) at 70°C in MeOH and EtOH with KOtBu (2 mol%) (S:C and TOF up to 25,000 and 14,000 h<sup>-1</sup>). The transfer hydrogenation (TH) of acetophenone in 2-propanol at reflux (S:C = 1000 and TOF up to 30,000 h<sup>-1</sup>) with alkali base (1–5 mol%) was catalysed by four out of the five complexes. HY and TH activity increases occurred after the addition of dinitrogen ligands to the first two complexes *in situ*.

### The Effect of N-Configurations on Selective Detection of Dopamine in the Presence of Uric and Ascorbic Acids using Surfactant-Free N-Graphene Modified ITO Electrodes

B. J. Matsoso, B. K. Mutuma, C. Billing, K. Ranganathan, T. Lerotholi, G. Jones and N. J. Coville, *Electrochim. Acta*, 2018, **286**, 29

The detection of dopamine (DA) in the presence of uric (UA) and ascorbic acids (AA) was explored using surfactant-free indium tin oxide (ITO) electrodes, modified with N-graphene films with differing N-configurations. XPS was used to characterise the films, composed of 38–60% pyridinic-N, 4–31% pyrrolic-N, 13–56% graphitic-N and 2–9% oxidised pyridinic-N (NO<sub>x</sub>). The NGr/ITO electrodes showed good selective electrocatalytic performance for the oxidation of DA in the presence of interferants (UA and AA), particularly the NGr-2/ ITO electrode with a detection limit (S:N=3) of DA of  $0.131 \pm 0.005 \mu\text{M}$ . This is attributed to improved  $\pi$ - $\pi$  interactions between the hydroxyl and amine groups on DA and the NO<sub>x</sub> (9.2%) and pyrrolic (59.6%) N-configurations.

### Influence of Filler Pore Structure and Polymer on the Performance of MOF-Based Mixed-Matrix Membranes for CO<sub>2</sub> Capture

A. Sabetghadam, X. Liu, M. Benzaqui, E. Gkaniatsou, A. Orsi, M. M. Lozinska, C. Sicard, T. Johnson, N. Steunou, P. A. Wright, C. Serre, J. Gascon and F. Kapteijn, *Chem. Eur. J.*, 2018, **24**, (31), 7949

The influence of metal-organic framework (MOF)

fillers and polymers on membrane performance was studied, in the context of separating CO<sub>2</sub> from N<sub>2</sub>. Four MOF materials (NH<sub>2</sub>-MIL-53(Al), MIL-69(Al), MIL-96(Al) and ZIF-94) and two polymers (6FDA-DAM and Pebax) were used to create eight unique composites with the MOFs acting as fillers and the polymers acting as matrices. Loading the composites with 25 wt% of MIL-96(Al) as a filler resulted in the best performance, increasing permeability to 32% and selectivity to 10% when combined with 6FDA-DAM. Similarly, when combining 25 wt% of MIL-96(Al) with Pebax, permeability was raised to 25% and selectivity to 18%.

### The Effect of Different Particle Residence Time Distributions on the Chemical Looping Combustion Process

M. A. Schnellmann, F. Donat, S. A. Scott, G. Williams and J. S. Dennis, *Appl. Energy*, 2018, **216**, 358

Chemical looping combustion (CLC) is an example of a reactor-regenerator system. A model for CLC was developed which describes two fluidised bed reactors with steady circulation particles between them. Investigations found that the process is sensitive to residence time distributions. By decreasing the variance of the residence time distribution under certain conditions, higher mean rates of reaction in the beds and greater mean conversion of the particles by the time they leave the reactors can be achieved. As a result, the circulation and inventory rate of solids could be reduced, leading to economic savings within the CLC process.