

Johnson Matthey Highlights

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

The Influence of Gas Composition on Pd-Based Catalyst Activity in Methane Oxidation – Inhibition and Promotion by NO

N. Sadokhina, G. Smedler, U. Nylén, M. Olofsson and L. Olsson, *Appl. Catal. B: Environ.*, 2017, **200**, 351

Methane oxidation on Pd and PtPd-based catalysts under lean conditions in the presence of either H₂O or NO is studied. 5 vol% H₂O severely inhibited the catalytic activity. Dry NO also suppressed catalytic activity. NO had a promotional effect on the activity when co-fed with water, compared to pure H₂O. It is proposed that NO reacts with hydroxyl species forming HNO₂ which reduced the deactivating effects of water present in the reaction mixture.

Selective Hydrogenation of Acetylene over Cu(211), Ag(211) and Au(211): Horiuti–Polanyi Mechanism vs. Non-Horiuti–Polanyi Mechanism

B. Yang, R. Burch, C. Hardacre, P. Hu and P. Hughes, *Catal. Sci. Technol.*, 2017, **7**, (7), 1508

DFT calculations are used to analyse and compare the Horiuti–Polanyi and non-Horiuti–Polanyi hydrogenation mechanisms for acetylene hydrogenation to ethylene over Cu(211), Ag(211) and Au(211). Hydrogen molecules dissociate first followed by the subsequent addition of hydrogen atoms to the hydrocarbon in the Horiuti–Polanyi mechanism whereas in the non-Horiuti–Polanyi mechanism, hydrogen molecules directly react with the hydrocarbon. The authors found that the Horiuti–Polanyi mechanism is preferred on Cu(211) for the hydrogenation reactions of acetylene to ethylene whereas the non-Horiuti–Polanyi mechanism is preferred for the reactions over Ag(211). In contrast, the hydrogenation of C₂H₂ and C₂H₃ on Au(211) follows the Horiuti–Polanyi mechanism, while the hydrogenation of C₂H₄ follows the non-Horiuti–Polanyi mechanism.

The Effect of Water on Methane Oxidation over Pd/Al₂O₃ under Lean, Stoichiometric and Rich Conditions

O. Mihai, G. Smedler, U. Nylén, M. Olofsson and L. Olsson, *Catal. Sci. Technol.*, 2017, **7**, (14), 3084

The effect of oxygen concentration and the presence of water on methane oxidation over a Pd/Al₂O₃ catalyst was investigated. This catalyst was characterised by BET, XRD, STEM, TPO and TPR. Various ramping experiments from 150–700°C were carried out using rich, stoichiometric and lean gas mixtures with and without water. Raising the oxygen concentration in a dry atmosphere resulted in higher methane oxidation activity which can be linked to the assistance of palladium oxide formation. Only small amounts of PdO up to 700°C were decomposed as shown by the TPO data but in the stoichiometric and rich reaction mixture, PdO was still decomposed due to the oxygen limitation.

A Parametric Evaluation of Powder Flowability Using a Freeman Rheometer Through Statistical and Sensitivity Analysis: A Discrete Element Method (DEM) Study

S. K. Wilkinson, S. A. Turnbull, Z. Yan, E. H. Stitt and M. Marigo, *Comp. Chem. Eng.*, 2017, **97**, 161

A case study simulating a Freeman rheometer to characterise powder flowability is presented. DEM was used with input parameters to describe static and rolling coefficients, coefficient of restitution, Young's modulus and cohesion energy density. DoS principles were used to create a simulation matrix to explore these. Basic flowability energy and specific energy were assessed. Static and rolling friction were found to play a critical role in determining powder basic flowability energy and specific energy while cohesion energy density affected basic flowability energy.

Porous Zinc and Cobalt 2-Nitroimidazolate Frameworks with Six-Membered Ring Windows and a Layered Cobalt 2-Nitroimidazolate Polymorph

A. Orsi, D. J. Price, J. Kahr, R. S. Pillai, S. Sneddon, S. Cao, V. Benoit, M. M. Łozińska, D. B. Cordes, A. M. Z. Slawin, P. L. Llewellyn, I. Casely, S. E. Ashbrook, G. Maurin and P. A. Wright, *CrystEngComm*, 2017, **19**, (10), 1377

Polymorphs of $Zn(2-nIm)_2$ and $Co(2-nIm)_2$ ($2-nIm = 2$ -nitroimidazole) were prepared by solvothermal synthesis or recrystallisation of ZIF-65(Zn/Co). The compounds produced were isostructural, with a tetrahedrally-connected framework topology similar to tridymite (lonsdaleite). Single crystal XRD analysis showed that $Zn(2-nIm)_2$ has rotational disorder for two of the three crystallographically-distinct linker types. Computation and solid-state NMR spectroscopy analysis were carried out. The compounds were tested for their uptake of CO_2 and selectivity for CO_2 over CH_4 and N_2 .

Effect of Crystallite Size on the Performance and Phase Transformation of Co_3O_4/Al_2O_3 Catalysts During CO-PrOx – an *in situ* Study

T. M. Nyathi, N. Fischer, A. P. E. York and M. Claeys, *Faraday Discuss.*, 2017, **197**, 269

The effect of crystallite size on the mass- and surface area-specific CO oxidation activity and the reduction behaviour of Co_3O_4 were studied. The reverse micelle technique was used to synthesise model Co_3O_4 catalysts with average crystallite sizes between 3 and 15 nm. During the catalytic tests, it was found that reducing the size of Co_3O_4 crystallites raised the mass-specific CO oxidation activity between 50–200°C. Moreover, in the same temperature range the surface area-specific CO oxidation activity demonstrated a volcano-type behaviour where crystallites with an average size of 8.5 nm were the most active. The reduction of Co_3O_4 was examined *in situ* by a magnetometer and a PXRD capillary cell while recording kinetic data.

Understanding the Unusual Reduction Mechanism of Pd(II) to Pd(I): Uncovering Hidden Species and Implications in Catalytic Cross-Coupling Reactions

C. C. C. Johansson Seechurn, T. Sperger, T. G. Scrase, F. Schoenebeck and T. J. Colacot, *J. Am. Chem. Soc.*, 2017, **139**, (14), 5194

In a large number of Pd-catalysed processes the reduction of Pd(II) intermediates to Pd(0) is a vital elementary step. In the case of P^tBu_3 , which is one of the most powerful new generation phosphine ligands, oxidation state Pd(I) and not Pd(0), is generated upon reduction from Pd(II). Experimental and computational studies were used to evaluate the mechanism of the reduction of Pd(II) to Pd(I) for the emergence of the highly active precatalyst

$\{Pd(\mu-Br)(P^tBu_3)\}_2$. The development of dinuclear Pd(I) as opposed to the Pd(0) complex $(P^tBu_3)_2Pd$ was demonstrated to be dependent on the stoichiometry of Pd to phosphine ligand, the order of adding the reagents and, most importantly, the nature of the Pd precursor and the option of the phosphine ligand used. Mechanistically vital additional Pd- and phosphine-containing species were identified by experiments on gram scale in Pd.

Nanoscale Ion Intermixing Induced Activation of Fe_2O_3/MnO_2 Composites for Application in Lithium Ion Batteries

S. Hao, B. Zhang, J. Feng, Y. Liu, S. Ball, J. Pan, M. Srinivasan and Y. Huang, *J. Mater. Chem. A*, 2017, **5**, (18), 8510

A facile method to produce hollow-structured oxygen-vacancy-rich Fe_2O_3/MnO_2 nanorods is demonstrated. The results show that oxygen vacancies are induced by nanoscale ion intermixing between Fe and Mn ions during annealing. Due to their distinct core-shell hollow nanostructure and the presence of oxygen vacancies the Fe_2O_3/MnO_2 nanorods display excellent electrochemical performances as anode material for lithium ion batteries and a reversible capacity higher than 700 mA h g^{-1} after 2000 cycles.

Superoleophobic Surface Modification for Robust Membrane Distillation Performance

N. G. P. Chew, S. Zhao, C. Malde and R. Wang, *J. Membrane Sci.*, 2017, **541**, 162

Robust membranes with anti-fouling and anti-wetting qualities are being investigated for produced water treatment from oil and gas industry by direct-contact membrane distillation (DCMD). In this work, a composite Janus membrane was prepared by single-step co-deposition of polydopamine (PDA)/polyethylenimine (PEI) onto the outer surface of a commercial hydrophobic polyvinylidene fluoride (PVDF) substrate. Its performance was tested by feeding a series of low surface tension solutions. This modified PVDF membrane, which was inspired by mussel adhesive, could potentially be used for long-term water recovery from produced water *via* DCMD.

Influence of Sb on the Structure and Performance of Pd-Based Catalysts: An X-ray Spectroscopic Study

S. Gatla, O. Mathon, A. Rogalev, S. Pascarelli, J. Radnik, M.-M. Pohl and A. Brückner, *J. Phys. Chem. C*, 2017, **121**, (7), 3854

XPS and XAFS investigations were carried out on 10 wt% Pd–16 wt% Sb/TiO₂ catalyst for gas-phase acetoxylation of toluene to benzyl acetate. The impact of the co-component Sb on the active Pd species was assessed. Excess electron charge was found on metallic Pd species after several hours on stream.

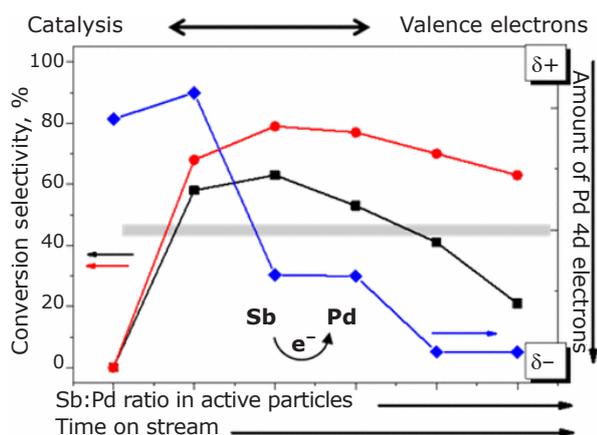
This phenomenon may be due to electron transfer from metallic Sb. TEM-EDX analysis confirmed that intermixed Pd-Sb particles with an atomic ratio of

5–6 were present in the most active catalysts and an atomic ratio of 3 in deactivated samples.

Synthesis and Characterization of Boron Carbon Oxynitride Films with Tunable Composition using Methane, Boric Acid and Ammonia

B. J. Matsoso, K. Ranganathan, B. K. Mutuma, T. Lerotholi, G. Jones and N. J. Coville, *New J. Chem.*, 2017, 41, (17), 9497

2D boron carbon oxynitride (BCNO) films were synthesised by atmospheric pressure chemical vapour deposition (APCVD) using carbon-rich methane, nitrogen-rich ammonia, boron- and oxygen-rich boric acid as precursors. Various atomic compositions were accomplished by altering the vapourisation temperature of boric acid by changing the distance (i.e. 2 cm to 12 cm) between boric acid and the growth substrate. The XPS survey spectra showed that the atomic compositions of the BCNO films formed differ as follows: C 48–71 at%, B 2.34–12.8 at%, N 1.98–7.9 at% and O 33–34 at%. The films also indicated vibrational modes from h-BN, B–C and graphene domains from Raman spectra.



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