

Johnson Matthey Highlights

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

EMISSION CONTROL TECHNOLOGIES

Formation of Reactive Lewis Acid Sites on Fe/WO₃-ZrO₂ Catalysts for Higher Temperature SCR Applications

R. Foo, T. Vazhnova, D. B. Lukyanov, P. Millington, J. Collier, R. Rajaram and S. Golunski, *Appl. Catal. B: Environ.*, 2015, **162**, 174

An active ammonia-SCR catalyst can be prepared by impregnating WO₃-ZrO₂ with Fe. WO₃-ZrO₂ containing Fe (in wt%) 0, 0.5, 2.3 and 10 was investigated and the relationship between the catalytic activity and surface acidity was studied by pyridine adsorption. 3 wt% Fe/WO₃-ZrO₂ is the most active and reduced NO_x by 10%–20% at 150°C and between 400°C and 550°C, 80%–85% conversion is achieved. New Fe³⁺ Lewis acid sites were formed and play an essential role by activating NO_x and increasing the strength of the Brønsted acidity.

Comparison of Different Kinetic Models for NO_x Storage on a Lean NO_x Trap

T. C. Watling, P. D. Bolton and D. Swallow, *Can. J. Chem. Eng.*, 2014, **92**, (9), 1506

The NO_x breakthrough curves were used to investigate the kinetics of NO_x storage on a lean NO_x trap (LNT). The measurements were taken using a laboratory reactor in a range of temperatures, from 125°C to 450°C. The breakthrough curves were performed until the saturation of LNT to: (a) allow NO oxidation to NO₂ to be researched in the absence of NO_x storage; (b) to allow the effective NO_x capacity as a function of temperature to be analysed; and (c) to provide a more demanding test for potential models. There are similarities of the breakthrough curves at 125°C and 450°C; at the beginning, there is a temperature independent portion followed by a temperature dependent portion which are explained by fast sites and slow sites. The amount of NO_x stored as a function of temperature was bell-shaped.

Parameter Estimation of a DOC from Engine Rig Experiments with a Discretized Catalyst Washcoat Model

B. Lundberg, J. Sjöblom, Å. Johansson, B. Westerberg and D. Creaser, *SAE Int. J. Engines*, 2014, **7**, (2), 1093

DOCs with varying compositions of Pt loading, washcoat thickness and volume were studied. Parameters were tuned against engine rig data, using specially selected engine operating points to illustrate the interplay between kinetics and mass transport. The resulting catalyst model included discretized washcoat as tanks in radial and axial series. For a catalyst model with internal transport resistance, it was found that some internal mass transport related parameters must be tuned in addition to the kinetic parameters. A model with little to no internal transport resistance could still have a good fit if kinetics parameters compensated for the transport limitations. It was important to use a kinetic model capable of describing exclusively intrinsic kinetics.

FINE CHEMICALS: CATALYSIS AND CHIRAL TECHNOLOGIES

Enzymatic Desymmetrising Redox Reactions for the Asymmetric Synthesis of Biaryl Atropisomers

S. Staniland, B. Yuan, N. Giménez-Agulló, T. Marcelli, S. C. Willies, D. M. Grainger, N. J. Turner and J. Clayden, *Chem. Eur. J.*, **20**, (41), 13084

The enantioselective synthesis of biaryl atropisomers with *ortho*-hydroxymethyl and formyl groups involves the oxidation of symmetrical diol substrates with a variant of galactose oxidase and the reduction of dialdehydes by a panel of ketoreductases. *M* or *P* enantiomers were produced and the absolute configurations were determined by time-dependent DFT calculations of circular dichroism spectra. The different biaryl structures have different selectivities which enables the active site of galactose oxidase to be analysed in detail.

Iridium-Catalyzed C-H Borylation of Heterocycles Using an Overlooked 1,10-Phenanthroline Ligand: Reinventing the Catalytic Activity by Understanding the Solvent-Assisted Neutral to Cationic Switch

C. C. C. Johansson Seechurn, V. Sivakumar, D. Satoskar and T. J. Colacot, *Organometallics*, 2014, **33**, (13), 3514

Borylation of *N*-Boc-indole at the 3-position with B₂pin₂ (pin = pinacolato) was achieved in consistent 99% yield

using 0.5 mol % of a preformed Ir catalyst, [Ir(Cl)(COD) (1,10-phenanthroline)] (2; COD = cyclooctadiene). This performance was substantially better than that of the corresponding *in situ* formed catalyst. This is thought to be due to formation of a competing inactive cationic complex 1 when carried out in a noncoordinating solvent such as octane. Using catalyst 2, the total synthesis of Meridianin G was accomplished in 87% overall isolated yield in a one-pot, three-step process.

NEW BUSINESSES: FUEL CELLS

Specific Adsorption of Perchlorate Anions on Pt{hk} Single Crystal Electrodes

G. A. Attard, A. Brew, K. Hunter, J. Sharman and E. Wright, *Phys. Chem. Chem. Phys.*, 2014, 16, (27), 13689

In this study, the specific adsorption of perchlorate anions on Pt{hk} electrodes (i.e. Pt{111}, Pt{100}, Pt{110} and Pt{311}) were analysed in perchloric acid electrolyte by cyclic voltammetry. The aim was to test a hypothesis made in recent publications of the adsorption of perchlorate anions on polycrystalline platinum. As the concentration of perchloric acid increased, both the OH_{ad} and electrochemical oxide states were notably perturbed for Pt{111}. This may be due to the competition of the perchlorate anions and OH_{ad} for the adsorption sites. The hydrogen underpotential deposition region of Pt{111} was unaffected but perchlorate anion decomposition to chloride on Pt{111} was observed. For Pt{100}, there was no difference in the onset of electrochemical oxide formation or any state in the potential of the OH_{ad} state. For Pt{110} and Pt{311} there were negligible changes in the onset of electrochemical oxide formation. The specific adsorption of perchlorate anions on Pt{111} had a detrimental effect on the ORR. These results confirm the previously reported findings.

PRECIOUS METAL PRODUCTS: CHEMICAL PRODUCTS

Pulsed Electrical Discharge Synthesis of Red Photoluminescence Zinc Oxide Nanoparticles

S. S. Su, I. T. H. Chang, W. C. H. Kuo, D. Price, Z. Pikramenou and J. Lead, *J. Nanopart. Res.*, 2014, 16, (9), 2611

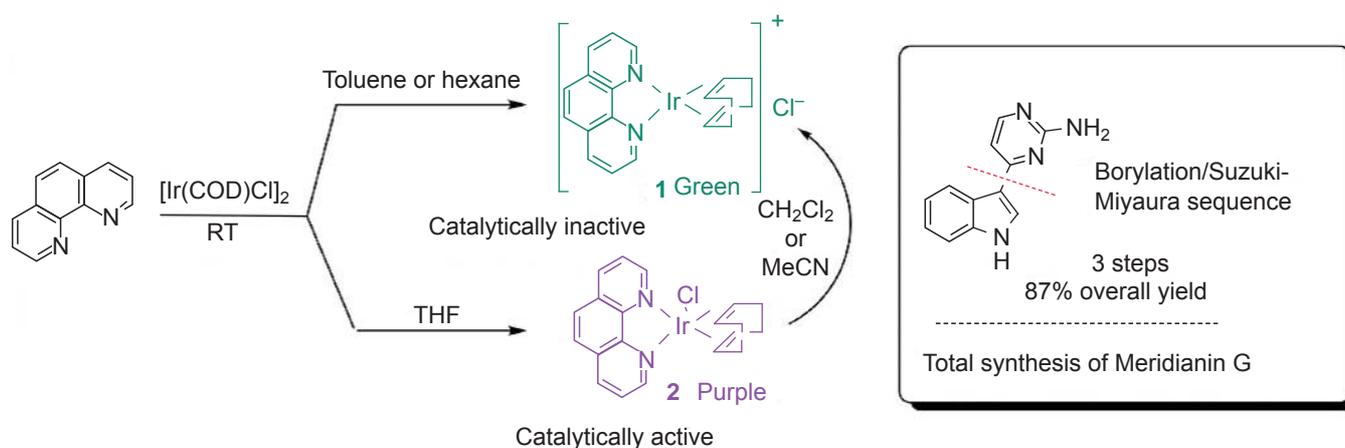
A pulsed electrical discharge in a liquid medium was used to synthesise ZnO nanoparticles which were then characterised using TEM, EDS and PL spectroscopy. The effects of the processing parameters such as liquid media, current, frequency of the electrical discharge and the electrode gap distance on the properties of the nanoparticles were investigated. The average size of the synthesised ZnO nanoparticles was between 10 nm and 25 nm. An increase in the arc current was found to notably increase the average particle size. The frequency of discharge and electrode gap distance can affect the average particle size and distribution due to a difference in the cooling rate. The as-synthesised ZnO nanoparticles display an ultraviolet emission of ~3.4 eV and a red visible emission of ~1.98 eV in the PL spectrum.

PROCESS TECHNOLOGIES

Assessment of Different Methods of Analysis to Characterise the Mixing of Shear-thinning Fluids in a Kenics KM Static Mixer using PLIF

F. Alberini, M. J. H. Simmons, A. Ingram and E. H. Stitt, *Chem. Eng. Sci.*, 2014, 112, 152

The blending of two non-Newtonian shear thinning fluids where a minor secondary flow is blended into a major primary flow was analysed using Kenics KM static mixers. The concentration distribution at the mixer outlet was determined using planar laser induced fluorescence (PLIF). The total fluid superficial velocity (0.1–0.6 m s⁻¹); pipe internal diameter (0.0127–0.0254 m);



C. C. C. Johansson Seechurn *et al.*, *Organometallics*, 2014, 33, (13), 3514

the volumetric flow ratio between the primary and secondary flows (10:1 and 25:1) and changing the rheology of the secondary flow have been investigated. The capability of the Kenics KM static mixer can be determined by the analysis of PLIF images using the traditional CoV, maximum striation area methods, the areal distribution method and the new individual striation method.

Upgrading Biomass Pyrolysis Vapors over β -zeolites: Role of Silica-to-Alumina Ratio

C. Mukarakate, M. Watson, J. ten Dam, X. Baucherel, S. Budhi, M. Yung, H. Ben, K. Lisa, R. M. Baldwin and M. R. Nimlos, *Green Chem.*, 2014, doi: 10.1039/C4GC01425A

The vapour phase upgrading of pine pyrolysis products was carried out in a flow microreactor using a range of β -zeolites with various silica-to-alumina ratios (21, 25, 38, 75, 250) with the aim of investigating how the acid sites affect product distribution, yields and coking. During the experiment, 40 discrete 50 mg batches of biomass were pyrolysed and the vapours were upgraded over 0.5 g of catalyst on a horizontal fixed bed semi-batch reactor. Products were measured by MBMS and py-GCMS. The authors found that aromatic hydrocarbons and olefins with no detectable oxygen-containing species were mainly produced when the catalyst was fresh for β -zeolites with a lower silica-to-alumina ratio (more acid sites). The fresh catalysts with a higher silica-to-alumina ratio (less acid sites) produced a range of oxygenated products i.e. furans, phenol and cresols.

Impact of Chemical Heterogeneity on the Accuracy of Pore Size Distributions in Disordered Solids

I. Hitchcock, S. Malik, E. M. Holt, R. S. Fletcher and S. P. Rigby, *J. Phys. Chem. C*, 2014, **118**, (35), 20627

The determination of pore size distribution (PSD) is important for developing structural models and understanding the activity and selectivity of heterogeneous catalysts. A new integrated gas sorption and mercury porosimetry technique was used to get complementary experimental data to the extensive studies recently carried out by simulations. A subset of pores was prepared within a disordered network of an amorphous material (e.g. silica or alumina) and the sorption behaviour of nitrogen and argon were compared. The heavy metal surface led to higher pressure in silica but not alumina. This was not the case for nitrogen.

A New Combined Nuclear Magnetic Resonance and Raman Spectroscopic Probe Applied to *In Situ* Investigations of Catalysts and Catalytic Processes

J. C. J. Camp, M. D. Mantle, A. P. E. York and J. McGregor, *Rev. Sci. Instrum.*, 2014, **85**, (6), 063111

In this study, Raman and nuclear magnetic resonance (NMR) spectroscopies were used together in a new single experimental probe which enables simultaneous measurements on the same sample to be recorded. The progress of a reaction can be monitored using the probe and the authors demonstrated this with the evolution of the homogeneously catalysed metathesis of 1-hexene. Magic angle spinning (MAS) NMR was also used with a custom made MAS 7 mm rotor which is able to spin up to 1600 Hz. This was applied to the heterogeneous metathesis of 2-pentene and ethene to investigate the structure-performance relationships.