

Johnson Matthey Highlights

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

EMISSION CONTROL TECHNOLOGIES

Low Temperature NO Storage of Zeolite Supported Pd for Low Temperature Diesel Engine Emission Control

H.-Y. Chen, J. E. Collier, D. Liu, L. Mantarosie, D. Durán-Martín, V. Novák, R. R. Rajaram and D. Thompsett, *Catal. Lett.*, 2016, **146**, (9), 1706

A simulated diesel engine exhaust gas feed was used to demonstrate the ability of a zeolite-supported Pd to adsorb NO at temperatures lower than 200°C. It is thought that the highly dispersed Pd on the zeolite exchange sites are the active sites. The NO storage capacity and NO_x desorption temperature are both strongly affected by the zeolite framework structure. It may be possible to apply the studied materials for low-temperature NO_x emission control.

Impact of Zeolite and γ -Alumina Intra-particle Diffusion on the Performance of a Dual Layer Catalyst

M. Dudák, V. Novák, P. Kočí, M. Marek, P. Blanco-García and D. Thompsett, *Chem. Eng. J.*, 2016, **301**, 178

The effect of diffusion limitation on the performance of a model dual-layer oxidation catalyst was studied. The samples include a bottom Pt/ γ -Al₂O₃ layer which is also coated with a top layer of either zeolite or alumina, both of these are of interest for automotive exhaust gas aftertreatment. The samples were analysed in a lab reactor for CO oxidation as a probe reaction and the scale of diffusion limitation on CO conversion was investigated. A 1D+1D model along with a 3D digital reconstruction of pore space was used to study the gas transport in dual layer systems, and the contribution of micro-, meso- and macro-pores to the overall transport and conversion was determined. The internal pore sizes of zeolites were an order of magnitude less compared to those found in γ -Al₂O₃, the outcome of this is a significantly different intra-particle diffusivity. The results from the analysed samples and performed parametric investigation show that the macropores in the coated layers represent a vital structural attribute which allow efficient transport.

FINE CHEMICALS

Intensified Biocatalytic Production of Enantiomerically Pure Halophenylalanines from Acrylic Acids using Ammonium Carbamate as the Ammonia Source

N. J. Weise, S. T. Ahmed, F. Parmeggiani, E. Sirola, A. Pushpanath, U. Schell and N. J. Turner, *Catal. Sci. Technol.*, 2016, **6**, (12), 4086

The novel combination of a cyanobacterial phenylalanine ammonia lyase (PAL) and ammonium carbamate reaction buffer was used to develop an intensified, industrially relevant procedure for synthesising enantiopure halophenylalanines. This method simplified catalyst/reaction buffer preparation and work up, and improved space-time yield (STY) to >200 g l⁻¹ d⁻¹ and ee \geq 98%.

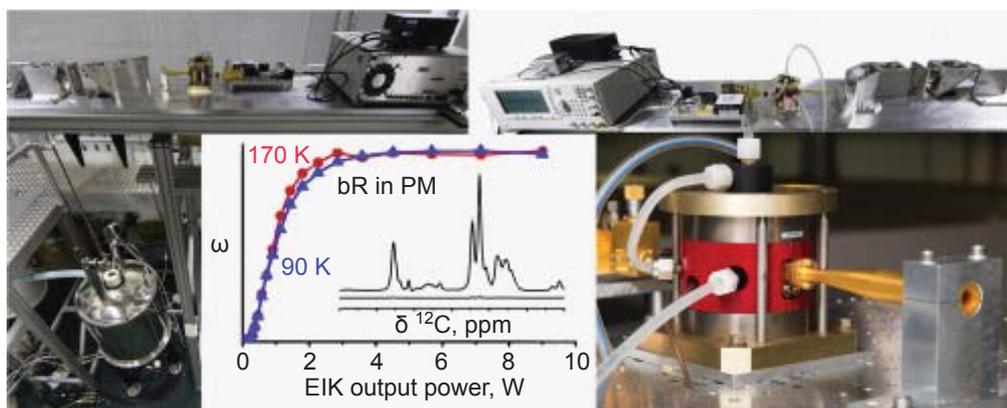
Dynamic Nuclear Polarization Enhanced NMR at 187 GHz/284 MHz using an Extended Interaction Klystron Amplifier

T. F. Kemp, H. R. W. Dannatt, N. S. Barrow, A. Watts, S. P. Brown, M. E. Newton and R. Dupree, *J. Magn. Res.*, 2016, **265**, 77

A DNP enhanced solid-state MAS NMR spectrometer with a EIK amplifier as the microwave source (see **Figure**) was developed and tested with a biomolecule, a pharmaceutical and a functionalised silica. The amplifier does not need a sweepable magnetic field due to its bandwidth, and is compact and easy to add to an existing spectrometer. The operating principle is briefly described. The maximum DNP enhancement requires less than 3 W output from the microwave source and the probe can operate down to 90 K at 8 kHz. The enhancement for the biomolecule was over 100 and for the pharmaceutical and the silica it was approximately 25. This can reduce the time for experiments that were previously too lengthy to carry out.

NEW BUSINESSES: BATTERY TECHNOLOGIES

Effect of Cation Structure on the Oxygen Solubility and Diffusivity in a Range of Bis{(trifluoromethyl)sulfonyl}imide Anion Based Ionic liquids for Lithium-air Battery Electrolytes



T. F. Kemp, H. R. W. Dannatt, N. S. Barrow, A Watts, S. P. Brown, M. E. Newton and R. Dupree, *J. Magn. Res.*, 2016, **265**, 77

A. R. Neale, P. Li, J. Jacquemin, P. Goodrich, S. C. Ball, R. G. Compton and C. Hardacre, *Phys. Chem. Chem. Phys.*, 2016, **18**, (16), 11251

The solubility and diffusivity of dissolved oxygen in a group of ionic liquids (IL) based on the bis{(trifluoromethyl) sulfonyl}imide anion with various related alkyl and ether functionalised cyclic alkylammonium cations were reported. The reduction of oxygen in IL at a microdisk electrode was observed using cyclic voltammetry; chronoamperometric measurements were applied to assess both the concentration and the diffusion coefficient of oxygen in different IL. Also included in this paper are the viscosity of the IL, the calculated molar volume and free volume. Within this class of IL, the oxygen diffusivity rises with declining viscosity of the neat IL. For the two IL families, an inverse relationship between oxygen solubility and IL free volume was outlined which suggests that oxygen is not residing in the accessible empty space.

Manganese Dissolution in Lithium-Ion Positive Electrode Materials

M. Saulnier, A. Auclair, G. Liang and S. B. Schougaard, *Solid State Ionics*, 2016, **294**, 1

A method for analysing Mn dissolution from Li-ion battery materials with no interference and good reproducibility is described. The detection limit is 50 ppb. A 1.0 M LiClO₄ and 1.0 M LiPF₆ in EC:DMC (1:1), LiFePO₄ were analysed as electrolytes, and two LiFe_{0.3}Mn_{0.7}PO₄ samples and a spinel LiMn₂O₄ were studied for comparison. The ageing was carried out only in electrolyte with and without forced oxidation. The Mn dissolution was found to be affected by water, free acid and the oxidative electrochemical potential.

NEW BUSINESSES: FUEL CELLS

Quantitative Energy-Dispersive X-Ray Analysis of Catalyst Nanoparticles Using a Partial Cross Section Approach

K. E. MacArthur, T. J. A. Slater, S. J. Haigh, D. Ozkaya, P. D. Nellist and S. Lozano-Perez, *Microsc. Microanal.*, 2016, **22**, (01), 71

New EDX detectors having higher count rates are used for quantitative elemental analysis via STEM. A method to calculate the partial cross section in order to quantify the EDX data is presented. This is useful as it is simple to apply. The method was tested by quantifying the Pt surface enrichment for acid-leached PtCo catalyst nanoparticles.

PROCESS TECHNOLOGIES

Effect of the Preparation Method of Supported Au Nanoparticles in the Liquid Phase Oxidation of Glycerol

N. Dimitratos, A. Villa, L. Prati, C. Hammond, C. E. Chan-Thaw, J. Cookson and P. T. Bishop, *Appl. Catal. A: Gen.*, 2016, **514**, 267

Stable Au nanoparticle catalysts in aqueous solution were prepared using NaBH₄ reduction of metal salts in the presence of PVA. Different particle size and distribution were possible by varying the ratio of polymer stabiliser to metal salt. The mean diameters ranged from 3–5 nm. Increased Au concentration led to increased diameter, as did decreasing the PVA concentration. However in the presence of PVA in the ratio PVA: Au = 2:1, there were larger particles probably due to partial aggregation and hence coalescence of the Au. Tests were carried out on liquid phase oxidation of glycerol to study the catalyst activity and selectivity, and this was found to be influenced by particle size and presence of protective agent.

Kinetics of Hg⁰ Oxidation over a V₂O₅/MoO₃/TiO₂ Catalyst: Experimental and Modelling Study under DeNOx Inactive Conditions

N. Usberti, S. A. Clave, M. Nash and A. Beretta, *Appl. Catal. B: Environ.*, 2016, **193**, 121

The effects of main operating variables such as temperature, HCl and Hg⁰ concentration were studied

as part of the kinetic investigation of mercury oxidation over a commercial plate type V/Mo/Ti/O catalyst. The experiment was performed under reference DeNOx inactive conditions. Both of the effects of temperature and HCl concentration showed that the conversion of Hg^0 was independent from the HCl content below 300–325°C, where the reaction demonstrated a positive temperature dependence; the conversion of Hg^0 became very sensitive to the HCl concentration at higher temperature. Therefore, the results indicate a strong dependence of the reaction kinetics on the surface coverage of HCl. A rate expression ($\text{Hg}^0 \rightarrow \text{HgCl}_{\text{ads}} \rightarrow \text{HgCl}_2$) was derived.

Sensitivity of Chemical-looping Combustion to Particle Reaction Kinetics

M. A. Schnellmann, S. A. Scott, G. Williams and J. S. Dennis, *Chem. Eng. Sci.*, 2016, **152**, 21

The authors study a simulation for chemical-looping combustion (CLC): two, coupled fluidised reactors with stable circulation of oxygen carrier particles between these. The sensitivity of CLC to various particle kinetics was assessed. When the average residence time is larger than the time for their complete reaction, the results indicate that the system is rather insensitive to different kinetics.

Influence of ZIF-8 Particle Size in the Performance of Polybenzimidazole Mixed Matrix Membranes for Pre-combustion CO_2 Capture and its Validation Through Interlaboratory Test

J. Sánchez-Laínez, B. Zornoza, S. Friebe, J. Caro, S. Cao, A. Sabetghadam, B. Seoane, J. Gascon, F. Kapteijn, C. Le Guillouzer, G. Clet, M. Daturi, C. Téllez and J. Coronas, *J. Membrane Sci.*, 2016, **515**, 45

The authors report the preparation and performance of mixed matrix membranes (MMM) based on polybenzimidazole (PBI) and ZIF-8 nanoparticles of

different mean sizes (50, 70 and 150 nm) as filler. At 150°C and feed pressures from 3–6 bar MMM comprising 10 and 20 wt% of ZIF-8 were analysed for H_2/CO_2 separation (pre-combustion CO_2 capture). There was a clear improvement in membrane performance with the addition of ZIF-8. A H_2 permeability rise of six times was observed after embedding 20 wt% of ZIF-8 along with an increase in the H_2/CO_2 selectivity by almost 55% compared to the bare PBI polymer membrane. When the filler size was increased there were improvements in both permeability and selectivity due to the smaller degree of agglomeration of the big particles which may be less active owing to their smaller exterior surface area. A better performance was shown in the MMM synthesised using dry 150 nm ZIF-8 filler compared to those containing wet filler. Aside from agglomeration problems favouring wet filler handling as indicated by infrared characterisation, preparing MMM with wet filler is straightforward compared with dry filler.

Process Improvements in Methanol Oxidation to Formaldehyde: Application and Catalyst Development

A. Andersson, J. Holmberg and R. Häggblad, *Top. Catal.*, 2016; doi:10.1007/s11244-016-0680-1

Historical developments leading to dramatic process intensification since the 1950s for the industrial scale oxidation of methanol to formaldehyde are described. The catalyst is an iron molybdate type catalyst which has retained the same basic chemical composition. The gains have been achieved in the productivity per reactor tube and per day. Novel catalysts containing Fe-(V)–Mo–O with spinel structure are also presented that offer a larger number of reoxidation sites (Fe) per Mo atom. The basic catalyst has selectivity of 92–95%.