

Johnson Matthey Highlights

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

EMISSION CONTROL TECHNOLOGIES

DOC Modeling Combining Kinetics and Mass Transfer using Inert Washcoat Layers

B. Lundberg, J. Sjöblom, Å. Johansson, B. Westerberg and D. Creaser, *Appl. Catal. B: Environ.*, 2016, **191**, 116

A kinetic and transport model for DOCs was developed. NO₂ was found to react preferentially with CO rather than C₃H₆. This causes NO oxidation to be inhibited. Experiments were carried out using inert washcoat layers of different thicknesses to resolve transport, kinetic and inhibition effects. The effect of washcoat transport resistance was clearest for the oxidation of C₃H₆ and CO. The kinetic model worked well when O, CO and NO₂ were the only surface species.

Study of Particulate Matter and Gaseous Emissions in Gasoline Direct Injection Engine using On-Board Exhaust Gas Fuel Reforming

M. Bogarra, J. M. Herreros, A. Tsolakis, A. P. E. York and P. J. Millington, *Appl. Energy*, 2016, **180**, 245

A prototype on-board fuel reformer was used in a GDI engine to investigate the effects of reformat combustion in addition to gasoline. The particulate and gaseous emissions were measured. 5%–6% lower fuel consumption and hence CO₂ emissions, was achieved by using the fuel reformer. Reformate could also reduce the engine PM emissions, depending on their nature with soot cores being removed more efficiently than volatile PM. A TWC also reduced the emissions of PM.

The Kinetics of Oxidation of Diesel Soots and a Carbon Black (Printex U) by O₂ with Reference to Changes in Both Size and Internal Structure of the Spherules during Burnout

C. J. Tighe, M. V. Twigg, A. N. Hayhurst and J. S. Dennis, *Carbon*, 2016, **107**, 20

At 450–550°C the rates of oxidation of two soots produced from burning either ultra low sulfur diesel or biodiesel in an engine, were measured with oxygen concentrations of 2.7–24.4 vol%; Printex U was also investigated. The volatile material from these carbons were removed by initially heating in argon; the resulting particles were found to burn in two steps. 20% of the

carbon in a soot particle was consumed in an initial, fast, transient reaction. During the second stage of burnout the rates of oxidation were in line with a model presuming these soots consist of porous spherules which burn throughout their interiors. The overall rates were half-order with respect to O₂ with an apparent activation energy of 145 ± 8 kJ mol⁻¹.

FINE CHEMICALS

Biocatalytic Dynamic Kinetic Resolution for the Synthesis of Atropisomeric Biaryl N-Oxide Lewis Base Catalysts

S. Staniland, R. W. Adams, J. J. W. McDouall, I. Maffucci, A. Contini, D. M. Grainger, N. J. Turner and J. Clayden, *Angew. Chem. Int. Ed.*, 2016, **55**, (36), 10755

Dynamic kinetic resolution (DKR) of rapidly racemising precursors showing free bond rotation was used to enantioselectively synthesise atropisomeric biaryl pyridine and isoquinoline N-oxides. The DKR was attained by ketoreductase (KRED) catalysed reduction of an aldehyde to form a configurationally stable atropisomeric alcohol, with a significant rise in rotational barrier emerging from the loss of a bonding interaction between the N-oxide and the aldehyde. The synthesis of either M or P enantiomer in excellent enantiopurity was possible by using various KRED. The asymmetric allylation of benzaldehyde derivatives with allyltrichlorosilane was catalysed by the enantioenriched biaryl N-oxide compounds.

Chemoselective Transfer Hydrogenation of α,β -unsaturated Carbonyl Compounds using Potassium Formate over Amine-grafted Ru/AIO(OH) Catalysts

Y. Gao, J. Wang, A. Han, S. Jaenicke and G. K. Chuah, *Catal. Sci. Technol.*, 2016, **6**, (11), 3806

An active and highly chemoselective heterogeneous catalyst was prepared by grafting 3-(2-aminoethylamino) propyltrimethoxysilane onto Ru/AIO(OH) and was used for the transfer hydrogenation of α,β -unsaturated carbonyl compounds to the equivalent allylic alcohols. The sustainable hydrogen donor was potassium formate. Various substrates cinnamaldehyde, α -amylcinnamaldehyde, citral, 3-methyl-2-butenal,

trans-2-pentenal and *trans*-hexenal were selectively hydrogenated at the C=O moiety with >96% selectivity. To compare, cinnamaldehyde was hydrogenated at the C=C bond using unmodified 1 wt% Ru/AlO(OH) catalyst and yielded 3-phenylpropanal as the product. 20–25% selectivity to cinnamyl alcohol was demonstrated by the higher loaded samples with 2–10 wt% Ru. Low coordination sites were found to be more selective to hydrogenation of the internal C=C than the terminal C=O bond.

FINE CHEMICALS: API MANUFACTURING

Convergent Synthesis of the Renin Inhibitor Aliskiren Based on C5–C6 Disconnection and CO₂H–NH₂ Equivalence

E. Cini, L. Banfi, G. Barreca, L. Carcone, L. Malpezzi, F. Manetti, G. Marras, M. Rasparini, R. Riva, S. Roseblade, A. Russo, M. Taddei, R. Vitale and A. Zanotti-Gerosa, *Org. Process Res. Dev.*, 2016, **20**, (2), 270

Aliskiren, the renin inhibitor, has been synthesised by a novel route involving a C5 and C6 disconnection for the first time. The C5 carbon acts as a nucleophile while a Curtius rearrangement is used to introduce the amine group. The C4 and C5 stereogenic centres are created simultaneously by an asymmetric hydrogenation step. The method is simple to operate, exhibits step economy and provides a good overall yield. It is considered suitable for scale manufacture.

Development of a Multi Kilogram-Scale, Tandem Cyclopropanation Ring-Expansion Reaction en Route to Hedgehog Antagonist IPI-926

B. C. Austad, A. B. Hague, P. White, S. Peluso, S. J. Nair, K. M. Depew, M. J. Grogan, A. B. Charette, L.-C. Yu, C. D. Lory, L. Grenier, A. Lescarbeau, B. S. Lane, R. Lombardy, M. L. Behnke, N. Koney, J. R. Porter, M. J. Campbell, J. Shaffer, J. Xiong, J. C. Helble, M. A. Foley, J. Adams, A. C. Castro and M. R. Tremblay, *Org. Process Res. Dev.*, 2016, **20**, (4), 786

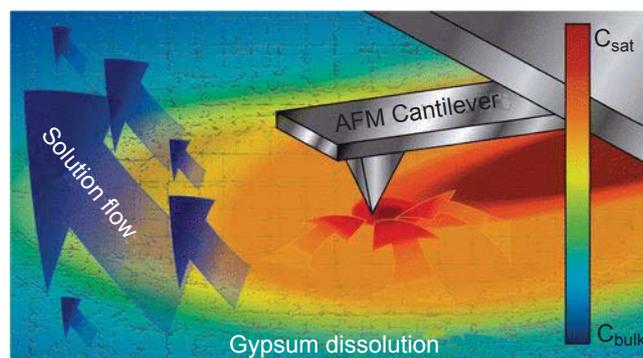
The semisynthesis of IPI-926 requires formation of a D-homocyclopropane ring system. This is done by chemoselective cyclopropanation followed by a stereoselective acid-catalysed carbocation rearrangement. New iodomethylzinc bis(aryl)phosphate reagents have been developed to achieve this step. They are soluble, prepared under mild conditions and remain stable during the reaction. They may also have favourable energetics compared to other alternatives such as EtZnCH₂I. The process optimisation investigations are explained in the present paper.

NEW BUSINESSES: FUEL CELLS

Importance of Mass Transport and Spatially Heterogeneous Flux Processes for *in Situ* Atomic Force Microscopy Measurements of Crystal Growth and Dissolution Kinetics

M. Peruffo, M. M. Mbogoro, M. Adobes-Vidal and P. R. Unwin, *J. Phys. Chem. C*, 2016, **120**, (22), 12100

This paper critically analyses literature data for gypsum dissolution to develop finite element method models to study the coupled mass transport-surface kinetic problem for dissolution processes in AFM. It was found that mass transport must be taken into account when carrying out *in situ* AFM on macroscopic surfaces. This applies even when the high-convection fluid cells are used. Dissolution kinetics of crystals was found to be influenced largely by other processes elsewhere on the surface.



Reprinted with permission from M. Peruffo, M. M. Mbogoro, M. Adobes-Vidal and P. R. Unwin, *J. Phys. Chem. C*, 2016, **120**, (22), 12100. Copyright (2016) American Chemical Society

PRECIOUS METAL PRODUCTS

Characterization of Platinum and Iridium Oxyhydrate Surface Layers from Platinum and Iridium Foils

B. Johnson, C. Ranjan, M. Greiner, R. Arrigo, M. E. Schuster, B. Höpfner, M. Gorgoi, I. Lauermaun, M. Willinger, A. Knop-Gericke and R. Schlögl, *ChemSusChem*, 2016, **9**, (13), 1634

Thin platinum and iridium hydrous oxide layers were created by electrochemically oxidising platinum and iridium polycrystalline foils through anodisation, and were examined by photoelectron spectroscopy during heating and time series (temperature-programmed spectroscopy). High-energy photoelectron spectroscopy was used to investigate the films which contain oxygen in the form of bound oxides, water and hydroxides. The Pt films were found to be unstable and started to degrade instantly after removing from the electrolyte to form core-shell structures with a metallic inner core and a hydrous oxide outer shell almost lacking of Pt. It might be possible to manufacture PtO_x phases with increased stability due to the proof for metastable intermediate states of degradation. Accelerated degradation is caused by heating the film to 100°C and this demonstrates that stoichiometric oxides such as PtO₂ or PtO are not the active species in the electrolyte. The Ir films have increased stability and higher surface Ir content and defect density can be lowered by gentle

heating at low temperatures. Although both layers are based on noble metals, their surface structures are notably dissimilar.

[A New Approach to Develop Palladium-modified Ti-based Alloys for Biomedical Applications](#)

C. Qiu, A. Fones, H. G. C. Hamilton, N. J. E. Adkins and M. M. Attallah, *Mater. Des.*, 2016, **109**, 98

Ti-6Al-4V (Ti64) with Pd was modified using a combination of a new powder mixing or coating method and SLM or HIP with the aim of further enhancing its corrosion resistance. Porosity, surface structure, microstructure and composition using optical microscopy, SEM, EDX and EMA were characterised for the modified alloy samples. The mechanical properties were measured *via* tensile tests and electrochemical tests were used to evaluate their corrosion properties. Pd was homogeneously distributed among the base Ti alloy powder particles without impairing their sphericity using a new physical powder mixing method. Pd was mostly situated at grain boundaries after HIPing while during SLM Pd has dissolved into the matrix. Increased laser scanning speed continuously raised both the porosity in the as-SLMed samples and surface roughness. Pd boosted corrosion resistance in 2 M HCl by moving the corrosion potential into the passive region of Ti64 but did not cause substantial improvement in tensile properties.

PRECIOUS METAL PRODUCTS: ADVANCED GLASS TECHNOLOGIES

[Liquid Crystals as Optical Amplifiers for Bacterial Detection](#)

C. Zafiu, Z. Hussain, S. Küpcü, A. Masutani, P. Kilickiran and E.-K. Sinner, *Biosens. Bioelectr.*, 2016, **80**, 161

Lipopolysaccharides (LPS) self-assembled into monolayers on top of liquid crystals are a simple model

to study the interface between LPS and bacteria. This is potentially useful for detection and screening. The LPS layers' stability depends largely on the choice of saccharides. Both gram-positive and gram-negative bacteria will interact with the LPS layer. The detection limits were a minimum of 500 cells per millilitre of solution while the detection time was less than 15 min.

PROCESS TECHNOLOGIES

[Structure-transport Relationships in Disordered Solids using Integrated Rate of Gas Sorption and Mercury Porosimetry](#)

A. Nepryahin, E. M. Holt, R. S. Fletcher and S. P. Rigby, *Chem. Eng. Sci.*, 2016, **152**, 663

New details on structure-transport relationships in disordered porous pellets were delivered by a new experimental method. The relative importance of specific sub-sets of pores to mass transport rates within the network of two disordered porous solids were investigated using integrated rate of adsorption and mercury porosimetry experiments. This was accomplished by assessing the relative rates of low pressure gas uptake into a network, both before and after a known set of pores was filled with frozen, entrapped mercury. The compaction pressure influences the relative contribution to overall mass transport made by the subset of the largest pores for the catalyst pellets which were formed by tableting. The spatial distribution of entrapped mercury was mapped by CXT and this showed that the relative importance of the sub-sets is linked to their level of pervasiveness across the pellet and whether they percolate to the centre of the pellet. The impact of manufacturing process parameters on pellet structure and mass transport properties can be comprehensively revealed using a combination of integrated mercury porosity, gas sorption and CXT.