

Johnson Matthey Highlights

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

Non-Enzymatic Glucose Sensing based on Hierarchical Platinum Micro-/Nanostructures

T. Unmüssig, A. Weltin, S. Urban, P. Daubinger, G. A. Urban and J. Kieninger, *J. Electroanal. Chem.*, 2018, **816**, 215

Stable and selective sensors at neutral pH are required for non-enzymatic glucose monitoring in the biomedical industry. Hierarchical platinum micro-/nanostructured electrodes show promise in such applications. For instance, amperometric glucose measurements demonstrated a 10,000-fold increase in sensitivity in comparison to unmodified electrodes. The hierarchical electrode morphology provides a selectivity mechanism depending on the reaction kinetics, leading to a 2000-fold improvement in the selectivity of glucose in the presence of interferants. Selectivity was further enhanced by low-frequency electrochemical impedance spectroscopy and signal stability was improved by the implementation of chronoamperometric protocols.

Industrial Computational Catalysis and its Relation to the Digital Revolution

G. Jones, *Nature Catal.*, 2018, **1**, (5), 311

The modern world is on the cusp of a digital revolution. Computational materials chemistry has been widely researched in the industrial sector over the last couple of decades and this area of research will be of importance to the field of catalysis. This article considers where computational catalysis has taken us thus far and how it fits into the digital revolution. An intrinsic link is made between computational catalysis and the future of digital materials development. It is noted that these methods will be implemented both for large-scale product development and at the local level of the specialist field.

Determination of Molybdenum Species Evolution during Non-Oxidative Dehydroaromatization of Methane and its Implications for Catalytic Performance

M. Agote-Arán, A. B. Kroner, H. U. Islam, W. A. Sławiński, D. S. Wragg, I. Lezcano-González and A. M. Beale, *ChemCatChem*, 2019, **11**, (1), 473

Operando X-ray absorption spectroscopy and high-resolution powder diffraction were used to study Mo/H-ZSM-5, focusing on the evolution of Mo species. Isolated Mo-oxo species attached to the zeolite framework at the straight channels were the most abundant species present after calcination. Mo partially carburised to intermediate MoC_xO_y species during reaction and fully carburised during longer reaction times, detaching from the zeolite and aggregating to form Mo_{1.6}C₃ clusters. These clusters then grew on the outer zeolite surface, leading to catalyst deactivation. Carbon deposition on the outer shell of the zeolite crystals also contributes to deactivation.

Simultaneous Chemical Vapor Deposition and Thermal Strengthening of Glass

P. Sundberg, L. Grund Bäck, R. Orman, J. Booth and S. Karlsson, *Thin Solid Films*, 2019, **669**, 487

Flat glass was thermally strengthened by heating for up to 20 minutes. During this process, transparent and amorphous Al₂O₃ thin films were applied *via in situ* metal organic chemical vapour deposition. Using the surface ablation cell employed with inductively coupled plasma atomic emission spectroscopy, it was determined that the Al₂O₃ content at the surface had doubled. During the surface reaction, sodium was shown to migrate to the surface to create a hazy layer which could be washed away with water. Increased crack resistance and increased surface hardness of the tempered glass at low indentation loads was achieved through the application of the Al₂O₃ films.

Catalyst-Based BS VI Stage 2 Emission Control Solutions for Light Duty Diesel

S. Sumiya, A. Kumar, J. Wylie and D. Bergeal, 'Catalyst-Based BS VI Stage 2 Emission Control Solutions for Light Duty Diesel', SAE Technical Paper 2019-26-0141, 2019

Various after-treatment systems for the light duty diesel market are being assessed for India BS VI Stage 1. The requirements for Stage 2 of the standards are still being discussed, but it is understood that real driving emission assessments will be introduced. It's likely that more robust emission control systems, such as those being developed for Euro 6d, will be required. Euro 6d system designs such as newly developed lean NOx trap (NSC) coatings used with selective catalytic reduction filters (SCR[®]) are described. They show potential as light duty diesel solutions for India BS VI Stage 2.

Operando and Postreaction Diffraction Imaging of the La-Sr/CaO Catalyst in the Oxidative Coupling of Methane Reaction

D. Matras, S. D. M. Jacques, S. Poulston, N. Grosjean, C. Estruch Bosch, B. Rollins, J. Wright, M. Di Michiel, A. Vamvakeros, R. J. Cernik and A. M. Beale, *J. Phys. Chem. C*, 2019, **123**, (3), 1751

X-ray diffraction computed tomography was used to study a La-Sr/CaO catalyst *operando* during the oxidative coupling of methane (OCM) reaction. The evolving solid-state chemistry was tracked during the temperature ramp, OCM reaction and after cooling using full-pattern Rietveld analysis. The main catalyst components (La₂O₃, CaO-SrO mixed oxide and SrCO₃) demonstrated stability in the initial reaction. The spatial distribution of the catalyst components is shown in **Figure 1**. A second CaO-SrO mixed oxide was formed by the decomposition of SrCO₃ to SrO after doubling the gas hourly space velocity. Vegard's law was applied during the Rietveld refinement to demonstrate the spatial variation of Sr occupancy in the mixed CaO-SrO oxides (**Figure 1(c)**). Increased catalyst basicity and an enhancement of the lattice oxygen diffusion are some of the benefits gained from Sr-doped CaO species formation.

Ion Exchange and Binding in Selenium Remediation Materials Using DNP-Enhanced Solid-State NMR Spectroscopy

M. Mais, J. Torroba, N. S. Barrow, S. Paul and J. J. Titman, *Solid State Nucl. Magn. Reson.*, 2019, **98**, 19

Dynamic nuclear polarisation (DNP) enhanced solid-state NMR was used to investigate selenate-loaded selenium water remediation materials. In comparison to conventional carbon-13 NMR spectra, DNP was shown to significantly reduce the

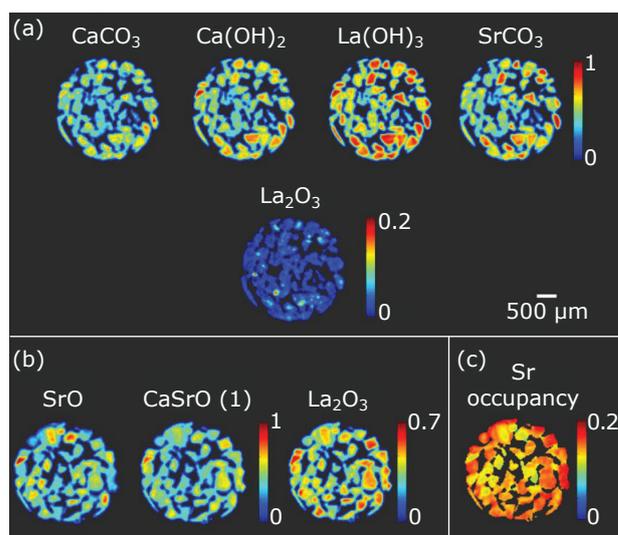


Fig. 1. (a) spatial distribution of the La-Sr/CaO catalyst components at room temperature; (b) spatial distribution of the La-Sr/CaO catalyst components at 780°C in He; (c) spatial distribution occupancy of Sr in mixed CaO-SrO (1) oxide. Reprinted with permission from D. Matras *et al.*, *J. Phys. Chem. C*, 2019, **123**, (3), 1751. Copyright 2019 American Chemical Society. Further permissions related to this material should be directed to the American Chemical Society

experiment time for carbon-13. This reduction enabled the efficient acquisition of $\{^1\text{H}\}\text{-}^{77}\text{Se}$ heteronuclear correlation spectra, even at relatively low Se concentrations. This demonstrated the nature of the binding of the remediated selenate ions. A supramolecular interaction with the functionalising polymer side chain is suggested.

Emission Control System Designing to Meet China 6

Q. Zhang, X. Ren, X. Wu, J. Li, C. Chen, J. Wang, Y. Sun, H. Ji and S. Chen, 'Emission Control System Designing to Meet China 6', SAE Technical Paper 2018-01-1706, 2018

China 6, consisting of China 6a (similar to Euro 6d) and China 6b, will be implemented from 1st July 2020. This presents a challenging situation for emission control system design. Three TWC systems with different pgm loadings were tested and the engineering target was met under fresh and aged conditions for systems with pgm loading $>40\text{ g ft}^{-3}$ for the front brick and 10 g ft^{-3} for the rear brick. Particle emissions were further reduced by using a coated GPF, which achieved 56% filtration efficiency under fresh conditions and 92% under aged conditions. This enabled the test vehicle to meet the China 6b requirements. Soot deposition and regeneration in the coated GPF were also studied.

Investigation of ZSM-5 Catalysts for Dimethylether Conversion using Inelastic Neutron Scattering

A. Zachariou, A. Hawkins, D. Lennon, S. F. Parker, Suwardiyanto, S. K. Matam, C. R. A. Catlow, P. Collier, A. Hameed, J. McGregor and R. F. Howe, *Appl. Catal. A: Gen.*, 2019, **569**, 1

Inelastic neutron scattering (INS) spectroscopy was used to analyse zeolite ZSM-5 catalysts used for the conversion of dimethylether to hydrocarbons. When INS was combined with NMR, it was shown that deactivation in dimethylether conversion occurred more rapidly than deactivation in methanol conversion. Lower levels of water present during dimethylether conversion is thought to be the cause of this rapid deactivation and is associated with the formation of less methylated aromatic coke species. This work demonstrates the ability of INS to probe lower frequency vibrational modes in a working catalyst without sample preparation.

Tunable Binding of Dinitrogen to a Series of Heterobimetallic Hydride Complexes

S. Lau, A. J. P. White, I. J. Casely and M. R. Crimmin, *Organometallics*, 2018, **37**, (23), 4521

Ruthenium main-group heterobimetallic complexes are generated *via* the reaction of $[\text{Ru}(\text{H})_2(\text{N}_2)_2(\text{PCy}_3)_2]$ with β -diketiminato stabilised hydrides of Al, Zn and Mg. The degree of binding of the diatomic ligand can be altered by changing the main-group fragment of $\text{M}\cdot\text{Ru}\text{-N}_2$ ($\text{M}=\text{Al}$, Zn, Mg) complexes in the order $\text{Al}<\text{Zn}<\text{Mg}$, which leads to a small decrease in the $\nu_{\text{N}=\text{N}}$ stretch. This is due to the increased ionic character of the metal-hydride bonding within the $\text{M}\cdot\text{Ru}\text{-N}_2$ complex, which is more prevalent with a less electronegative metal. The increased ionic character leads to destabilisation of the frontier molecular orbitals of ruthenium, which in turn allows for increased $\text{Ru}(4d) \rightarrow \pi^*(\text{N}-\text{N})$ back-donation.

Polyvinylidene Fluoride Membrane Modification via Oxidant-Induced Dopamine Polymerization for Sustainable Direct-Contact Membrane Distillation

N. G. P. Chew, S. Zhao, C. Malde and R. Wang, *J. Membr. Sci.*, 2018, **563**, 31

Accelerated oxidant-induced polydopamine (PDA) deposition on the inner and outer surfaces of a porous hydrophobic polyvinylidene fluoride (PVDF) membrane was used to fabricate a composite PVDF membrane with sandwich structure. The PDA-decorated membrane was evaluated by bench-scale direct-contact membrane distillation experiments. The membrane demonstrated flux enhancement up to 70% in 3.5 wt% NaCl solution at 333 K. The PDA-decorated membrane also maintained a stable flux and high salt rejection rate when used for seawater desalination and exhibited good fouling- and wetting-resistant properties. A potential application for the membrane would be water recovery from industrial wastewater containing low surface tension substances.

MnPO₄-Coated Li(Ni_{0.4}Co_{0.2}Mn_{0.4})O₂ for Lithium (-Ion) Batteries with Outstanding Cycling Stability and Enhanced Lithiation Kinetics

Z. Chen, G.-T. Kim, D. Bresser, T. Diemant, J. Asenbauer, S. Jeong, M. Copley, R. J. Behm, J. Lin, Z. Shen and S. Passerini, *Adv. Energy Mater.*, 2018, **8**, (27), 1801573

The authors propose MnPO₄-coated LiNi_{0.4}Co_{0.2}Mn_{0.4}O₂ (MP-NCM) as a cathode material for use in lithium-ion batteries. The MnPO₄ coating was chosen to physically prevent contact between the NCM active material and the electrolyte by acting like a protective layer. This protective layer helps to stabilise the electrode/electrolyte interface and prevents the occurrence of detrimental side reactions. This results in enhanced rate capability and outstanding cycling stability.