

Johnson Matthey Highlights

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

On-Board Generation of Hydrogen to Improve In-Cylinder Combustion and After-Treatment Efficiency and Emissions Performance of a Hybrid Hydrogen–Gasoline Engine

J.-C. Martin, P. Millington, B. Campbell, L. Barron and S. Fisher, *Int. J. Hydrogen Energy*, 2019, **44**, (25), 12880

Hydrogen on-board fuel reforming was identified as a waste energy recovery technology. H₂ and carbon monoxide were added to a conventional exhaust gas recirculation (EGR) system to simulate a reformed EGR (rEGR) system. Specific concentrations of H₂ and CO were chosen to be achievable at typical gasoline exhaust temperatures. The rEGR system was shown to be a viable commercial option capable of stabilising combustion, improving engine efficiency and reducing harmful emissions. The calorific value of the fuel was shown to increase by 28% as the result of complete fuel reformation.

Continuous Flow Aerobic Oxidation of Benzyl Alcohol on Ru/Al₂O₃ Catalyst in a Flat Membrane Microchannel Reactor: An Experimental and Modelling Study

G. Wu, E. Cao, P. Ellis, A. Constantinou, S. Kuhn and A. Gavriilidis, *Chem. Eng. Sci.*, 2019, **201**, 386

An experimental and theoretical study was performed on a flat Teflon AF-2400 membrane microchannel reactor for alcohol oxidation on a 5 wt% Ru/Al₂O₃ catalyst. Separated gas and liquid channels ensured a continuous supply of oxygen throughout the experiment and helped to prevent the mixing of gaseous oxygen with organic reactants. Experimental data from a catalyst stability test were used to estimate the kinetics of benzyl alcohol oxidation with a 2D reactor model. A theoretical study was performed on mass transfer and catalytic reaction in the membrane microchannel reactor and the controlling process was found to be oxygen transverse mass transport in the catalyst bed.

Evaluation of Operational Cycles for Long-Term Run of a Tar Removal Catalytic System

C. P. B. Quitete, V. L. Ximenes, A. M. Steele and M. M. V. M. Souza, *Chem. Eng. Technol.*, 2019, **42**, (5), 980

Early deactivation of catalysts during the tar removal step of biomass gasification experiments is an issue at the pilot and demo scale. To prevent this, a method was developed using toluene as a tar model compound in a bench-scale micro activity unit. A commercial Pt catalyst with Ce-Zr-Al supports was used. Regeneration and reactivation periods were alternated with nitrogen, hydrogen and steam. Operational cycles were used for toluene steam reforming to reach a long-term run. The results from this work will benefit pilot-plant studies and impact regeneration and reactivation procedures.

4D Visualisation of *in situ* Nano-Compression of Li-Ion Cathode Materials to Mimic Early Stage Calendering

S. R. Daemi, X. Lu, D. Sykes, J. Behnsen, C. Tan, A. Palacios-Padros, J. Cookson, E. Petrucco, P. J. Withers, D. J. L. Brett and P. R. Shearing, *Mater. Horiz.*, 2019, **6**, (3), 612

Lithium-ion battery electrodes are calendered after manufacturing and the influence of this on the resulting microstructure is relatively unknown. A novel technique is presented to 3D-image battery electrodes *in situ* during uniaxial compression using X-ray nano-computed tomography. A combination of novel sample preparation techniques, a nano-mechanical stage and digital volume correlation allowed the electrode strain to be tracked during compression (**Figure 1**). This work provides insight into the mechanical behaviour of electrodes and into the industrial calendering process. Further study and understanding in these areas will lead to design and performance optimisation of Li-ion electrodes.

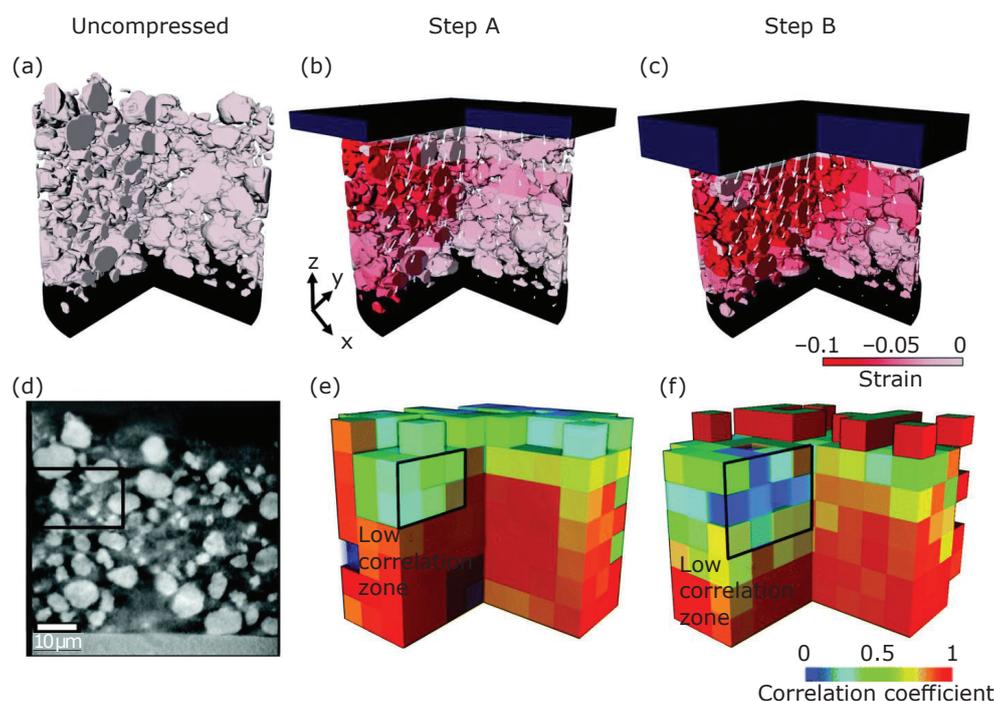


Fig. 1. (a–c) surface rendering of the sample with the strain mapped on the surface as well as the vector field in the z-direction representative of each slice; (d) virtual slice of the uncompressed dataset; (e) and (f) volume rendering of the correlation coefficient (CC) map, given by the average CC for each correlation sub-volume. The black box highlights the same low correlation zone in all images. Published by The Royal Society of Chemistry.

Modeling, Development, and Testing of a 2 MW Polymeric Electrolyte Membrane Fuel Cell Plant Fueled with Hydrogen from a Chlor-Alkali Industry

S. Campanari, G. Guandalini, J. Coolegem, J. ten Have, P. Hayes and A. H. Pichel, *J. Electrochem. Energy Convers. Storage*, 2019, **16**, (4), 041001

Hydrogen is produced as a byproduct of the chlor-alkali industry and this has the potential to feed a PEM fuel cell. In this study, a large-scale (2 MW) PEM fuel cell power plant fuelled with hydrogen is installed at the site of chlor-alkali manufacturing. The plant is first modelled to allow for the study of different operational strategies and to find the optimal operating setpoint for the plant. The model also predicts fuel cell stack behaviour and simulates pressure drops, auxiliary consumptions and operating conditions of components. The model is validated by experimental results. Indicators such as hydrogen consumption, energy production and efficiency are discussed.

Syngas Conditioning by Ceramic Filter Candles Filled with Catalyst Pellets and Placed Inside the Freeboard of a Fluidized Bed Steam Gasifier

E. Savuto, A. Di Carlo, A. Steele, S. Heidenreich, K. Gallucci and S. Rapagnà, *Fuel Process. Technol.*, 2019, **191**, 44

Syngas is produced from organic wastes *via* gasification. This process also generates unwanted byproducts such as tar and particulates which can

hinder the utilisation of the syngas. This study aimed to remove these byproducts by inserting a ceramic filter candle filled with nickel-catalyst pellets into a bench-scale fluidised bed reactor. Tests lasting 4 h were performed with the candle partially and fully filled with the catalyst. Different operating conditions were also examined. The best results were observed for a partially filled candle at high temperatures, with residual tar reduced to 250 mg Nm^{-3} . Deactivation of the Ni-catalyst was not observed during the tests.

Efficient Experimental Approach to Evaluate Mass Transfer Limitations for Monolithic DOCs

M. Walander, J. Sjöblom, D. Creaser, B. Lundberg, S. Tamm and J. Edvardsson, *Top. Catal.*, 2019, **62**, (1–4), 391

Monolithic DOCs ($\text{Pt}/\gamma\text{-Al}_2\text{O}_3$) were used to study internal mass transfer limitations during NO oxidation using a synthetic-gas catalyst test bench. Internal mass transfer limitations were evaluated by experimental data obtained *via* a quick and straightforward test method. The ratio of reaction time constant to washcoat diffusion time constant helped to identify the temperatures where the transition between a kinetically controlled region and an internal mass transfer control region occurred in the DOCs. Internal mass transfer significantly limited NO conversion at 175°C for an average washcoat thickness of $110 \mu\text{m}$.

Structural Selectivity of Supported Pd Nanoparticles for Catalytic NH₃ Oxidation Resolved Using Combined Operando Spectroscopy

E. K. Dann, E. K. Gibson, R. H. Blackmore, C. R. A. Catlow, P. Collier, A. Chutia, T. E. Erden, C. Hardacre, A. Kroner, M. Nachtegaal, A. Raj, S. M. Rogers, S. F. R. Taylor, P. Thompson, G. F. Tierney, C. D. Zeinalipour-Yazdi, A. Goguet and P. P. Wells, *Nature Catal.*, 2019, **2**, (2), 157

The selectivity of supported Pd catalysts to N₂ was investigated using *operando* X-ray absorption fine structure spectroscopy, on-line mass spectrometry and diffuse reflectance infrared Fourier-transform spectroscopy. High N₂ selectivity was observed due to the insertion of nitrogen into the Pd nanoparticle structure at low temperatures (<200°C). At high temperatures (>280°C) adsorbed nitrates form at the surface of bulk PdO nanoparticles and this is linked to the unwanted formation of NO. Selective catalytic oxidation of NH₃ to N₂ is a potential resolution for the abatement of unused NH₃-based reductants from diesel exhaust after treatment and this study has clarified the selectivity-directing structure of supported Pd catalysts for this process.

Fluoride Binding by an Anionic Receptor: Tuning the Acidity of Amide NH Groups for Basic Anion Hydrogen Bonding and Recognition

R. Montis, A. Bencini, S. J. Coles, L. Conti, L. Fusaro, P. A. Gale, C. Giorgi, P. N. Horton, V. Lippolis, L. K. Mapp and C. Caltagirone, *Chem. Commun.*, 2019, **55**, (19), 2745

A family of bis-amide receptors containing carboxylic acid groups close to the amide function are presented, for the purpose of anion binding. The acidity of amide NH groups was shown to decrease with deprotonation of the carboxylic acids. The anion binding ability of the deprotonated receptors was then activated and the receptors had a selectivity for fluoride complexation. The proposed systems in this study demonstrate a novel example of anionic receptors able to bind anions through H-bonding.

On the High Structural Heterogeneity of Fe-Impregnated Graphitic-Carbon Catalysts from Fe Nitrate Precursor

R. Arrigo and M. E. Schuster, *Catalysts*, 2019, **9**, (4), 303

This study used near-edge X-ray absorption fine structure spectroscopy, core-level X-ray photoelectron spectroscopy and atomic resolution electron microscopy to investigate graphite-supported Fe-based materials from Fe nitrate precursors. A number of different chemical phases, particle sizes and morphologies were

identified. Large agglomerates of an oxy-hydroxide ferrihydrite-like phase were observed together with thermally stable single atoms and few atoms clusters. Transformation of the poorly ordered oxy-hydroxide phase into several oxide phases was induced thermally. Thermally stable N impurities were retained in the structure as Fe-N-O bonds. The high heterogeneity identified in these catalysts can be explained by the structural dynamic induced by thermal treatment and the nature of interactions with the support.

Experimental and Computational Study of DOC on CSF for Heavy Duty Diesel Applications

S. Sethuraman, S. Sitamraju, Y. M. Lopez-De Jesus and P. Markatou, SAE Technical Paper 2019-01-0586, SAE International, Warrendale, USA, 2nd April, 2019

The performance benefits and challenges of DOC on CSF were investigated by comparison with a DOC + CSF system and a DOC + bare DPF system. The DOC on CSF was optimised for passive soot oxidation and NO oxidation performance and the underlying mechanisms of the technology were demonstrated using simulations and experimental data. In comparison to DOC + CSF and DOC + DPF, the passive soot oxidation characteristics of DOC on CSF were similar or better under certain conditions. The DOC on CSF demonstrated lower active regeneration efficiency, the result of increasing temperatures along the length of the part during fuel injection.

Investigation of the Dynamics of 1-Octene Adsorption at 293 K in a ZSM-5 Catalyst by Inelastic and Quasielastic Neutron Scattering

A. P. Hawkins, A. J. O'Malley, A. Zachariou, P. Collier, R. A. Ewings, I. P. Silverwood, R. F. Howe, S. F. Parker and D. Lennon, *J. Phys. Chem. C*, 2019, **123**, (1), 417

Inelastic neutron scattering (INS) and quasielastic neutron scattering (QENS) were used to study the properties of 1-octene adsorbed in zeolite ZSM-5 at 293 K to understand interactions related to the zeolite solid acid catalysis of fluidised catalytic cracking reactions. At ambient temperatures, significant changes of bonding on adsorption were observed between the INS spectrum and those recorded for the solid alkene. This can be credited to the formation of a medium chain *n*-alkane or *n*-alkane cation *via* oligomerisation of the adsorbed 1-octene. A temperature-dependant fraction of the oligomers can rotate around their long axis within the pore channels. This was demonstrated through QENS analysis.