

Johnson Matthey Highlights

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

Cohesive Strength Measurement of Catalyst Layer: Uniform Drying and On-Line Monitoring

J. Yang, E. M. Holt, K. Huang, P. Blanco-García A. Wagland, M. J. Hounslow and A. D. Salman, *Chem. Eng. Res. Des.*, 2018, **132**, 1117

Automotive catalyst coatings are generally deposited on the inside walls of a ceramic or metallic monolith. The strength of the coating layer is an important consideration to improve lifetime and activity levels of the catalytic converter. Both cohesive and adhesive failure modes are possible for the coated catalyst layer. A method to quantify the individual cohesive strength using a uniform drying system is proposed here. The behaviour was observed using on-line monitoring of a washcoat layer drying process. It was found that the cohesive strength varies with particle size, pH of catalyst suspension and drying rate of the suspension.

Formation of Size-Dependent and Conductive Phase on Lithium Iron Phosphate During Carbon Coating

Y. Liu, J. Liu, J. Wang, M. N. Banis, B. Xiao, A. Lushington, W. Xiao, R. Li, T.-K. Sham, G. Liang and X. Sun, *Nature Commun.*, 2018, **9**, 929

Carbon coating by pyrolysis of an organic substance on lithium iron phosphate particles at high temperature is used to improve conductivity in active materials for Li-ion batteries. However the process causes formation of secondary phases. The conductive phase was observed during coating and was found to be dependent on size, temperature and annealing atmosphere. Its formation depends on the reducing capacity in the carbon coating process. The work is expected to enable control of phase composition and tuning of the quality during manufacture.

Effect of Mixing Conditions on the Wet Preparation of Ceramic Foams

A. Celani, S. Blackburn, M. J. H. Simmons and E. H. Stitt, *Chem. Eng. Res. Des.*, 2018, **134**, 1

Scale-up of ceramic foams was studied using an agitated baffled vessel fitted with an up-pumping pitch blade turbine and a bottom round sparger. The effect of mixing parameters on the foam properties was determined. Flow conditions were carried out in low to mid transitional regime. DoE was used to create the screening experiments with different sparging time, air flow rate, impeller speed and impeller diameter. Rheology results were found to be useful for at-line measurement to control the structure of the material produced.

Ideal Versus Real: Simulated Annealing of Experimentally Derived and Geometric Platinum Nanoparticles

T. Ellaby, J. Aarons, A. Varambhia, L. Jones, P. Nellist, D. Ozkaya, M. Sarwar, D. Thompsett and C.-K. Skylaris, *J. Phys.: Condens. Matter*, 2018, **30**, (15), 155301

The structures of commercially available Pt catalysts were determined using electron microscopy and are here compared with geometric cuboctahedral and truncated octahedral structures using classical and quantum atomistic simulations. The potential energy surface at different temperatures and the effect of annealing on catalytic activity on nanoparticles with different geometries and sizes was examined using a simulated annealing procedure. Annealing both experimental and geometric nanoparticles produced structures similar in shape and predicted activity, using oxygen adsorption as a measure. Annealing is predicted to increase the catalytic activity in all cases except the truncated octahedra, where it has the opposite effect.

Performance of Preformed Au/Cu Nanoclusters Deposited on MgO Powders in the Catalytic Reduction of 4-Nitrophenol in Solution

R. Cai, P. R. Ellis, J. Yin, J. Liu, C. M. Brown, R. Griffin, G. Chang, D. Yang, J. Ren, K. Cooke, P. T. Bishop, W. Theis and R. E. Palmer, *Small*, 2018, **14**, (13), 1703734

Au/Cu alloy nanoclusters were prepared by sputtering and gas phase condensation and deposited on MgO powders. These supported nanoparticles were active for the solution-phase catalytic reduction of 4-nitrophenol at room temperature. Costs are reduced compared to pure Au nanoparticles. EDX and aberration-corrected STEM were used to confirm the alloy structure which contained randomly placed Au and Cu atoms. The mixed alloys were found to be more active than either Au-rich or Cu-rich particles. This demonstrates that the interaction at the surface between Au and Cu seems to enhance the activity.

Identification of Carbon Species on Iron-Based Catalysts During Fischer-Tropsch Synthesis

D. Peña, A. Cognigni, T. Neumayer, W. van Beek, D. S. Jones, M. Quijada and M. Rønning, *Appl. Catal. A: Gen.*, 2018, **554**, 10

Carbon species on a commercial iron-based Fischer-Tropsch synthesis catalyst were studied using *in situ* XANES, *in situ* DRIFTS, TPH-MS, GC-MS and STEM-EDX. Re-oxidation or transformation of the active Hägg iron carbide phase did not lead to deactivation under the applied conditions. Sintering of this phase occurred over time on stream with increasing temperatures due to a hydrothermally-assisted process. Carbon species such as aliphatic hydrocarbons from wax and oxygenate compounds such as alcohols, aldehydes, ketones and carboxylates were on the catalyst surface. Carboxylate species resisted hydrogenation at 280°C and the strongly adsorbed carbon species remaining on the catalyst surface from wax products were mainly α -olefins and branched carboxylic species.

Ru/ZrO₂ Catalysts for Transfer Hydrogenation of Levulinic Acid with Formic Acid/Formate Mixtures: Importance of Support Stability

Y. Gao, H. Zhang, A. Han, J. Wang, H.-R. Tan, E.-S. Tok, S. Jaenicke and G.-K. Chuah, *ChemistrySelect*, 2018, **3**, (5), 1343

Levulinic acid was transfer hydrogenated to γ -valerolactone using equimolar formate/formic acid in water and Ru/ZrO₂ catalysts. Ru/ZrO₂ with loadings <3 wt% were more active than those with higher loadings. Catalyst stability was investigated. A sol-gel process was used to prepare the catalysts in order to prevent metal leaching by trapping the Ru particles in the support. However the catalyst

became deactivated after one run. There was no agglomeration of Ru particles although the ZrO₂ support was found to have converted from predominantly tetragonal crystal to monoclinic phase and there was a decrease in the surface Ru/Zr ratio. Doping with 0.1 wt% SiO₂ stabilised the tetragonal phase of zirconia and enabled the catalyst to retain its activity.

Improving Biomass Pyrolysis Economics by Integrating Vapor and Liquid Phase Upgrading

K. Iisa, D. J. Robichaud, M. J. Watson, J. ten Dam, A. Dutta, C. Mukarakate, S. Kim, M. R. Nimlos and R. M. Baldwin, *Green Chem.*, 2018, **20**, (3), 567

In this perspective article, a combination of approaches for partial deoxygenation of bio-oil by catalytic fast pyrolysis with subsequent coupling and hydrotreating are investigated in detail. Some oxygen is removed during catalytic fast pyrolysis and the remainder removed by downstream hydrotreating, accompanied by carbon-carbon coupling reactions in either the vapour or liquid phase to improve carbon efficiency toward value-driven products (fuels or chemicals). The economic impact of partial deoxygenation by catalytic fast pyrolysis is explored as an integrated part of a two-stage process. Finally, including production of high-value co-products will be examined as a method of improving the overall pyrolysis-based biorefinery economics.

Operando Spectroscopy Study of the Carbon Dioxide Electro-Reduction by Iron Species on Nitrogen-Doped Carbon

C. Genovese, M. E. Schuster, E. K. Gibson, D. Gianolio, V. Posligua, R. Grau-Crespo, G. Cibir, P. P. Wells, D. Garai, V. Solokha, S. Krick Calderon, J. J. Velasco-Velez, C. Ampelli, S. Perathoner, G. Held, G. Centi and R. Arrigo, *Nature Commun.*, 2018, **9**, 935

Electrochemical reduction of CO₂ may be a route to C-C coupling to produce platform chemicals and represents the biggest challenge to this route. Nanostructured iron(III) oxyhydroxide on N-doped C support can be used to produce high Faraday efficiency and selectivity to acetic acid at low potential. Electron microscopy, *operando* X-ray spectroscopy and DFT simulations were used to correlate the activity to N-coordinated iron(II) sites. Evolution of H₂ could be correlated to the formation of metallic Fe and was the dominant reaction path.

Development of Suitable CuO-Based Materials Supported on Al₂O₃, MgAl₂O₄, and ZrO₂ for Ca/Cu H₂ Production Process

L. Díez-Martín, G. Grasa, R. Murillo, A. Scullard and G. Williams, *Ind. Eng. Chem. Res.*, 2018, **57**, (8), 2890

CuO-based materials supported on Al₂O₃, MgAl₂O₄ and ZrO₂ were prepared by different routes. Their performance for sorption enhanced reforming for H₂ production coupled to a Cu/CuO chemical loop was tested. The Al₂O₃ or MgAl₂O₄ supported materials synthesised by coprecipitation and mechanical mixing with Cu load ~65 wt% were stable. However ZrO₂ was not suitable for coprecipitation under these conditions. Pellets with high chemical and mechanical stability, high oxygen transport capacity and good mechanical properties were prepared by coprecipitation and can be scaled up.

[A One-Dimensional Model for Square and Octo-Square Asymmetric Particulate Filters with Correct Description of the Channel and Wall Geometry](#)

T. Watling, SAE Technical Paper, 2018-01-0951, 2018

This paper presents the first model to correctly describe the geometry of square and octo-square asymmetric particulate filters (PF), where the inlet channel is wider than the outlet channel in order to accommodate ash. Expressions are presented to describe the solid fraction of the PF, channel cross section and perimeter for both clean and soot/

ash loaded conditions. The error introduced by assuming the inlet channels are square rather than octahedral depends on the substrate, but can be significant. Pressure drop across the wall and soot cake are also provided.

[Effects of H₂S and Phenanthrene on the Activity of Ni and Rh-Based Catalysts for the Reforming of a Simulated Biomass-Derived Producer Gas](#)

D. Laprune, D. Farrusseng, Y. Schuurman, F. C. Meunier, J. A. Z. Pieterse, A. M. Steele and S. Thorpe, *Appl. Catal. A: Environ.*, 2018, **221**, 206

Rh and Ni-based catalysts for reforming methane and phenanthrene were tested. The feed composition was designed to replicate the producer gas from wood gasification. Phenanthrene was used to represent tar. H₂S was added at the higher range of typical values. At 900°C, 200 ppm of H₂S caused much greater loss of methane reforming activity than that caused by 200 ppm of phenanthrene. The rate of methane consumption in the presence of both poisons varied linearly with the Rh metal surface area. The rate of methane consumption per unit of metal surface area was about five times higher on Rh than on Ni.