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Johnson Matthey Highlights

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

EMISSION CONTROL TECHNOLOGIES

Is Reactor Light-Off Data Sufficiently Discriminating Between Kinetic Parameters to be Used for Developing Kinetic Models of Automotive Exhaust Aftertreatment Catalysts? The Effect of Hysteresis Induced by Strong Self Inhibition

J. E. Etheridge and T. C. Watling, *Chem. Eng. J.*, 2015, **264**, 376

Kinetic parameters used to predict CO oxidation over a diesel oxidation catalyst were found to give different results over a vehicle test cycle compared to a test reactor. This is thought to be due to two factors: dependence on the concentration of CO, since the reaction is strongly inhibited by CO; and hysteresis during temperature ramping up and down. This may be solved by using ramp down reactor data as well as ramp up reactor data; however this leads to the problems of discretising the data for ramp down into a much larger number of elements, and the fact that hysteresis does not always occur.

Model-Based Experimental Screening for DOC Parameter Estimation

B. Lundberg, J. Sjöblom, Å. Johansson, B. Westerberg and D. Creaser, *Comp. Chem. Eng.*, 2015, **74**, 144

A new method of estimating both kinetic and mass transport parameters was investigated for a DOC on a full-scale engine rig. Data screening by sensitivity analysis was applied, selecting different subsets using multivariate data analysis (MVDA) on a large transient data set. Principal component analysis (PCA) and D-optimal onion design were used to continuously update the data subset. The proposed method achieved a 32% lower residual sum of squares but was also less likely to converge to a local minimum. However it also took significantly more time than the alternative methods.

The Effect of Pt:Pd Ratio on Heavy-Duty Diesel Oxidation Catalyst Performance: An Experimental and Modeling Study

B. M. Shakya, B. Sukumar, Y. M. López-De Jesús and P. Markatou, SAE 2015 World Congress & Exhibition, 21st–23rd April, 2015, Detroit, Michigan, USA, SAE Paper no. 2015-01-1052

The effect of the Pt:Pd ratio on DOCs was investigated by both experiment and modelling. The pgm loadings were <50 g ft^{-3}. Transient light-off and steady state experiments were carried out over hydrothermally aged DOCs and increasing the ratio of Pt:Pd was found to increase the oxidation of both *n*-decane and NO, although the oxidation of unsaturated C3 and C7 HCs levelled off at higher Pt:Pd ratios. The higher Pd catalysts exhibited better activity for CO oxidation. In addition, HCs lowered the outlet NO_2:NOx ratio due to reduction of NO_2 to NO.

FINE CHEMICALS: CATALYSIS AND CHIRAL TECHNOLOGIES

Interstitial Modification of Palladium Nanoparticles with Boron Atoms as a Green Catalyst for Selective Hydrogenation

C. W. A. Chan, A. H. Mahadi, M. M.-J. Li, E. C. Corbos, C. Tang, G. Jones, W. C. H. Kuo, J. Cookson, C. M. Brown, P. T. Bishop and S. C. E. Tsang, *Nature Commun.*, 2014, **5**, 5787

The modification of the Pd/$CaCO_3$ lindlar catalysts with lead acetate and quinoline are commonly used for the partial hydrogenation of alkynes but there are limitations because lead is toxic and there is a risk of leaching. In this study Pd was modified below the surface to produce an ultra-selective nanocatalyst. Boron atoms are located in the Pd interstitial lattice sites and are chemically and thermally stable due to a strong host-guest electronic interaction after treating supported Pd nanoparticles with a borane tetrahydofuran solution. The subsurface boron atoms alter the adsorptive properties of Pd and demonstrate ultra-selectivity in some demanding alkyne hydrogenation reactions.

NEW BUSINESSES: FUEL CELLS

Low Temperature Growth of Carbon Nanotubes on Tetrahedral Amorphous Carbon using Fe–Cu Catalyst

R. Cartwright, S. Esconjauregui, D. Hardeman, S. Bhardwaj, R. Weatherup, Y. Guo, L. Arsié, B. Bayer, P. Kidambi, S. Hofmann, E. Wright, J. Clarke, D. Oakes, C. Cepek and J. Robertson, *Carbon*, 2015, **81**, 639

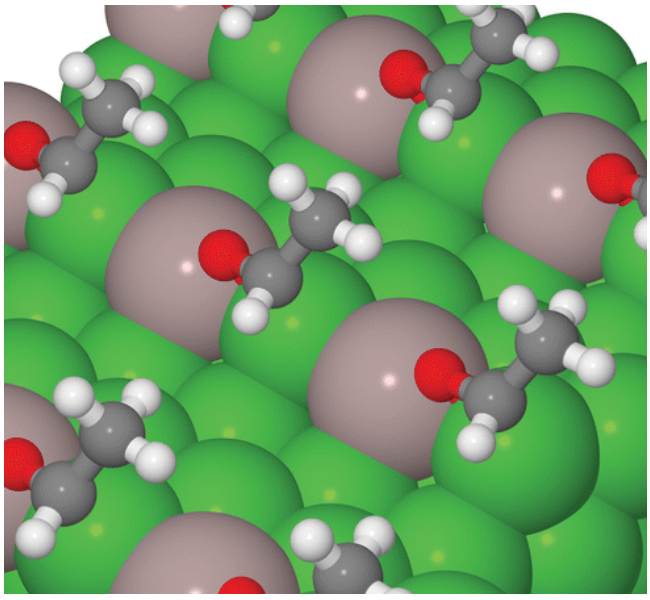
Carbon nanotubes are grown on tetrahedral amorphous (sp^3 rich) carbon by a CVD process using a Fe-Cu catalyst at <500ºC. Cu decreases the temperature at which the reduction of Fe occurs. The catalytic activity of Fe for the nucleation of nanotubes at low temperatures is improved and at the same time its tendency to diffuse into the carbon substrate is reduced resulting in minimal damage to the support. This study shows that nanotubes can be directly grown on the carbon fibres and can, therefore, be used in composites and fuel cell electrodes.

PROCESS TECHNOLOGIES

Origin of Catalytic Activity in Sponge Ni Catalysts for Hydrogenation of Carbonyl Compounds

G. Jones, *Catal. Struct. React.*, 2015, 00, 1

The activity of sponge Ni catalysts is affected by Al and other dopants. The direct reduction of acetaldehyde as a test system was investigated and a kinetic model for this reaction is constructed using density functional theory (DFT). The catalytic performance of carbonyl hydrogenation was enhanced by Al due to the increased reactivity towards O containing molecules and the affinity towards C was simultaneously decreased. In this study, the author compared this test system to acetylene hydrogenation where the activity depends on the C affinity of the catalysts. Early transition metal dopants may aid the selectivity of the hydrogenation of a carbonyl group in the presence of an alkene. The intrinsic electronic structure of the dopant was found to be responsible for the change in catalytic activity.



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Innovative Oxygen Carriers Uplifting Chemical-looping Combustion

T. Mattisson, J. Adánez, K. Mayer, F. Snijkers, G. Williams, E. Wesker, O. Bertsch and A. Lyngfelt, *Energy Procedia*, 2014, **63**, 113

There is no gas separation stage required in chemical looping combustion, therefore, this removes the high energy penalty and costs associated with other carbon capture techniques. The authors investigate chemical-looping combustion with gaseous fuels rich in methane in this EU funded project, Innovative Oxygen Carriers Uplifting Chemical-Looping Combustion (INNOCUOUS). Viable alternative oxygen carriers with low or no Ni are required due to the high cost of Ni-based materials and special environmental/safety precautions. This study focuses on the preparation and testing of oxygen carrier; two oxygen carriers of $CaMn_xTi_yMg_{1-x-y}O_3$ were produced by spray-drying and an oxygen carrier of Fe_2O_3/Al_2O_3 was produced by impregnation. The Ca-based material displayed promising results in a 10 kW and 120 kW unit and complete combustion was achieved.

Development of Mixed Matrix Membranes Containing Zeolites for Post-combustion Carbon Capture

N. Bryan, E. Lasseuguette, M. van Dalen, N. Permogorov, A. Amieiro, S. Brandani and M.-C. Ferrari, *Energy Procedia*, 2014, **63**, 160

A solvent casting method was used to synthesise mixed matrix membranes from poly(amide-b-ethylene oxide) (PEBAX MH1657) and zeolite 13X for CO_2/N_2 separation. A constant volume–variable pressure method was used to determine the gas permeation properties of neat PEBAX membranes and 5 wt%, 10 wt% and 15 wt% of zeolite 13X loadings for pure CO_2 and N_2. An increased loading of zeolite 13X resulted in a higher CO_2 permeability and at the maximum loading, the CO_2/N_2 selectivity was 47.

Direct Steam Reforming of Diesel and Diesel-Biodiesel Blends for Distributed Hydrogen Generation

S. Martin, G. Kraaij, T. Ascher, P. Baltzopoulou, G. Karagiannakis, D. Wails and A. Wörner, *Int. J. Hydrogen Energy*, 2015, **40**, (1), 75

Diesel and 7 vol% biodiesel blends were directly steam reformed at different operating conditions: reformer temperature, feed mass flow rate and diesel sulfur content. A precious metal based catalyst was used. Low catalyst inlet temperatures and high feed mass flow rates adversely affect the catalyst activity. However the long term performance of the precious metal catalyst tested with a desulfurised diesel-biodiesel blend showed an improvement. A stable product gas composition close to chemical equilibrium was attained over 100 h on stream by using diesel with 1.6 parts per million weight (ppmw) sulfur at a catalyst inlet temperature of >800ºC, a steam-to-carbon ratio of 5 and a feed mass flow per open area of catalyst of 11 g h^{-1} cm^{-2}.

Discrete Element Method (DEM) for Industrial Applications: Comments on Calibration and Validation for the Modelling of Cylindrical Pellets

M. Marigo and E. Hugh Stitt, *KONA Powder Particle J.*, 2015, **32**, 236

DEM is increasingly being used for simulation of complex processes. In order to extend its usefulness into more industrial application areas, the present study has investigated a test case involving cylindrical pellets represented by conjoined spheres in a “sand pile test”. The input parameters were calibrated, validated and optimised along with the shape representation. Two configurations of rotating drum system were simulated, one with a single baffle and one unbaffled. The results were compared with experimental data. The qualitative results compared well, however there were significant errors in the quantitative results. Further work is needed to improve the evaluation protocols for estimating key properties of particles, and better understand the quality of fit in such models.

The Effect of Solvent and Temperature in the Synthesis of CPO-27-Ni by Reflux

J. Guasch, P. D. C. Dietzel, P. Collier and N. Acerbi, *Micropor. Mesopor. Mater.*, 2015, **203**, 238

A Ni-based MOF, CPO-27-Ni, was synthesised by reflux at temperatures up to 110ºC using various mixtures of organic solvent (THF, 2-butanone, hexanol, *n*-butanol, ethylene glycol and glycerol), with water or water alone. The size and morphology of the crystal growth are affected by the choice of solvent. The same organic solvent/water mixture was tested at various temperatures and an effect on crystallisation and crystal morphology was observed. The large scale synthesis of CPO-27-Ni is feasible by the reflux method.

Proxy-based Accelerated Discovery of Fischer-Tropsch Catalysts

P. Boldrin, J. R. Gallagher, G. B. Combes, D. I. Enache, D. James, P. R. Ellis, G. Kelly, J. B. Claridge and M. J. Rosseinsky, *Chem. Sci.*, 2015, **6**, (2), 935

Heterogeneous catalysts for Fischer-Trospch synthesis were characterised using simple high-throughput techniques (XRD and TGA) to determine the particle size, surface area and reducibility both before and after an accelerated ageing test. A series of catalysts with good stability and high surface area with Mg and Ru promoters was determined using this procedure; their structural effects and how this affects the modes of deactivation was analysed. The combined use of the techniques enabled an increase in throughput of catalyst characterisation of up to 100 times and therefore, generated data on thousands of hours of stability testing time each month.