

Johnson Matthey Highlights

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

Structural Changes in Cartilage and Collagen Studied by High Temperature Raman Spectroscopy

M. Fields, N. Spencer, J. Dudhia and P. F. McMillan, *Biopolymers*, 2017, **107**, (6), e23017

High temperature Raman spectra for freeze-dried cartilage samples which demonstrate a rise in laser-excited fluorescence interpreted as conformational changes corresponding to denaturation above 140°C are reported. Spectra for separated collagen and proteoglycan fractions extracted from cartilage show the changes are linked with collagen. At high temperature peptide hydrolysis occurs suggesting that molecular H₂O is retained within the freeze-dried tissue as shown by the Raman data. Thermogravimetric analysis supports this hypothesis and shows 5–7 wt% H₂O remaining within freeze-dried cartilage that is gradually released upon heating up to 200°C. The capacity of the denatured collagen to re-absorb water is diminished and is shown by the spectra attained after exposure to high temperature and re-hydration following recovery.

Tailoring the Physical and Catalytic Properties of Lanthanum Oxycarbonate Nanoparticles

C. Estruch Bosch, M. P. Copley, T. Eralp, E. Bilbé, J. W. Thybaut, G. B. Marin and P. Collier, *Appl. Catal. A: Gen.*, 2017, **536**, 104

Lanthanum oxide and its carbonate analogues were synthesised by flame spray pyrolysis (FSP). Two different feeds were investigated: an organic solution and an aqueous organic microemulsion. The properties of the materials prepared are effected by a key experimental parameter of FSP, the O₂ dispersion i.e. the flow rate of the dispersing gas in the FSP nozzle. When a lanthanum containing organic solution was used as FSP feed, a rise in the level of O₂ dispersion led to a rise in surface area and a reduction in mean particle size and basicity. Lanthanum can form different phases, for example, oxides, hydroxides, oxycarbonates and carbonates. The rise of O₂ dispersion also initiated a phase change, going from a mixture of type Ia and type II La₂O₂CO₃ and La₂O₃ to pure La₂O₃. Using an aqueous or organic microemulsion feed which had a higher viscosity compared to the organic feed, produced materials with a lower surface area and a

higher mean particle size than those prepared using the organic solution at the same O₂ dispersion. In this case a mixture of type II La₂O₂CO₃ and La₂O₃ was attained. The materials were assessed for oxidative coupling of methane (OCM) and the authors were able to show that by changing the synthesis parameters, the OCM performance of the materials could be altered.

Reforming Biomass Derived Pyrolysis Bio-oil Aqueous Phase to Fuels

C. Mukarakate, R. J. Evans, S. Deutch, T. Evans, A. K. Starace, J. ten Dam, M. J. Watson and K. Magrini, *Energy Fuels*, 2017, **31**, (2), 1600

The catalytic conversion of the biogenic carbon in pyrolysis aqueous phase streams to produce hydrocarbons using a vertical microreactor coupled to a molecular beam mass spectrometer (MBMS) was investigated. Real-time analysis of products and tracking catalyst deactivation are provided by the MBMS. The HZSM-5 catalyst was used in this work, which improved the oxygenated organics in the aqueous fraction from noncatalytic fast pyrolysis of oak wood to fuels containing small olefins and aromatic hydrocarbons. The HZSM-5 catalyst showed higher activity and coke resistance during processing of the aqueous bio-oil fraction compared to similar experiments using biomass or whole bio-oils. Decreased coking was possible due to a release of coke precursors from the catalyst pores that was improved by excess process water available for steam stripping.

Lithium and Boron as Interstitial Palladium Dopants for Catalytic Partial Hydrogenation of Acetylene

I. T. Ellis, E. H. Wolf, G. Jones, B. Lo, M. M.-J. Li, A. P. E. York and S. C. E. Tsang, *Chem. Commun.*, 2017, **53**, (3), 601

It has been shown that light elements, including lithium and boron atoms, can reside in the octahedral (interstitial) site of a Pd lattice by altering the electronic properties of the metal nanoparticles, and therefore the adsorptive strength of a reactant. The obstruction of the sub-surface sites to H in the altered materials resulted in substantially increased selectivity for the partial catalytic hydrogenation of acetylene to ethylene.

Structure–Activity Relationship of Different Cu–Zeolite Catalysts for NH₃–SCR

M. P. Ruggeri, I. Nova, E. Tronconi, J. E. Collier and A. P. E. York, *Top. Catal.*, 2016, **59**, (10–12), 875

Three different catalytic materials for NH₃–SCR applications were investigated and its activities and selectivities towards undesired products (for example, N₂O and NH₄NO₃) were compared. The selected materials included a large pore Cu-BETA catalyst and two small pore structures: a Cu-CHA and a Cu-SAPO material, and were characterised by the same Cu loading. The objective was to study the potential impact of the microporous structure of the catalyst on the SCR performances.

Effect of Graphene Support on Large Pt Nanoparticles

L. G. Verga, J. Aarons, M. Sarwar, D. Thompsett, A. E. Russell and C.-K. Skylaris, *Phys. Chem. Chem. Phys.*, 2016, **18**, (48), 32713

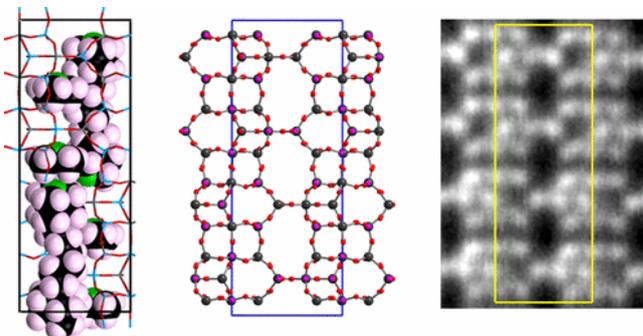
Pt clusters with up to 309 atoms interacting with single graphene supports with up to 880 carbon atoms were simulated by large-scale DFT calculations. The adsorption, cohesion and formation energies of two and three-dimensional Pt clusters interacting with the support, including dispersion interactions *via* a semi-empirical dispersion correction and a vdW functional were computed. When interacting with the support, three-dimensional Pt clusters are more stable than the two-dimensional and the difference between their stabilities increases with the system size. As the nanoparticle size is increased, the dispersion interactions are more pronounced and this is crucial to a reliable description of larger systems. The overall charge is transferred from the Pt clusters to the support as interatomic expansion (contraction) on the closest (farthest) Pt facets from the graphene sheet and charge redistribution were observed.

STA-20: An ABC-6 Zeolite Structure Prepared by Co-Templating and Solved *via* a Hypothetical Structure Database and STEM-ADF Imaging

A. Turrina, R. Garcia, A. E. Watts, H. F. Greer, J. Bradley, W. Zhou, P. A. Cox, M. D. Shannon, A. Mayoral, J. L. Casci and P. A. Wright, *Chem. Mater.*, 2017, **29**, (5), 2180

Dual templating by diDABCO-C6A and trimethylamine was used to prepare a novel microporous silicoaluminophosphate with topology STA-20 (see **Figure**). A hypothetical zeolite database and ADF-STEM with Rietveld refinement were used to resolve its structure. The zeolite structure STA-20 is a member of the ABC-6 family and it has trigonal symmetry, P-31c, with $a = 13.15497(18)$ Å and $c = 30.5833(4)$ Å in the calcined form. The stacking sequence is 12 layers of 6-rings (6Rs), AABAABAACAAC(A), containing single and double 6R units. STA-20 has a 3D-connected pore system limited by 8R windows and the longest cage

observed in an ordered ABC-6 material. Elemental analysis, ¹³C MAS NMR, computer modelling and Rietveld refinement were combined to obtain models for the location of the templates within cages of the framework.



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Enhancing the Thermoelectric Properties of Single and Double Filled *p*-Type Skutterudites Synthesized by an Up-Scaled Ball-Milling Process

J. Prado-Gonjal, P. Vaquero, C. Nuttall, R. Potter and A. V. Powell, *J. Alloy. Compd.*, 2017, **695**, 3598

Mechanical alloying was used to prepare single and double filled *p*-type skutterudites Ce_{0.8}Fe₃CoSb₁₂ and Ce_{0.5}Yb_{0.5}Fe_{3.25}Co_{0.75}Sb₁₂. It is a rapid method for preparing skutterudites that could be scaled up to industrial level. Enhanced figures of merit ZT were found for large-scale samples prepared by ball-milling compared with those prepared by conventional solid-state reaction. ZT rises ca. 19% at room temperature due to reduced grain size leading to reduced thermal conductivity. Effect of microstructure on thermoelectric properties, stability in air and performance after multiple heating and cooling cycles are presented. Improved resistance to oxidation are found in the densified samples prepared by ball-milling starting at 694 K for Ce_{0.8}Fe₃CoSb₁₂ and at 783 K for Ce_{0.5}Yb_{0.5}Fe_{3.25}Co_{0.75}Sb₁₂.

A New Type of Scaling Relations to Assess the Accuracy of Computational Predictions of Catalytic Activities Applied to the Oxygen Evolution Reaction

L. G. V. Briquet, M. Sarwar, J. Mugo, G. Jones and F. Calle-Vallejo, *ChemCatChem*, 2017, **9**, (7), 1261

Explicit water solvation and functionals that account for van der Waals interactions were used to modify the adsorption energies included in a DFT model to improve predictions for the overpotentials for the oxygen evolution reaction (OER) on RuO₂ and IrO₂. These are known experimentally to be similar and quite low but

widely used computational electrochemistry models based on adsorption thermodynamics do not show this. In such models IrO₂ is usually predicted to have low overpotentials while RuO₂ is predicted to have large overpotentials. The results of the present study explain the discrepancy and successfully predicted both oxides to be highly active.

On the Motion of Linked Spheres in a Stokes Flow

F. Box, E. Han, C. R. Tipton and T. Mullin, *Exp. Fluids*, 2017, **58**, (4), 29

Inspired by the mechanics of swimming microorganisms, the motion of linked spheres at low Reynolds number is being investigated. In the present study small permanent magnets were embedded in the spheres and an external magnetic field was applied to generate torques. Pairs of neutrally buoyant spheres connected by glass rods or thin elastic struts were found to move in a reciprocal orbit driven by an oscillatory field. Three spheres linked by elastic struts were observed to buckle in a periodic, non-reciprocal fashion. This effect propels the elemental swimmer with swimming direction determined by the geometrical asymmetry of the device. The technique may be suitable for miniaturisation.

A New Class of Cu/ZnO Catalysts Derived from Zincian Georgeite Precursors Prepared by Co-Precipitation

P. J. Smith, S. A. Kondrat, P. A. Chater, B. R. Yeo, G. M. Shaw, L. Lu, J. K. Bartley, S. H. Taylor, M. S. Spencer, C. J. Kiely, G. J. Kelly, C. W. Park and G. J. Hutchings, *Chem. Sci.*, 2017, **8**, (3), 2436

A Cu/ZnO catalyst was prepared from a zincian georgeite precursor synthesised by co-precipitation from acetate salts and ammonium carbonate. The presence of Zn plus mild ageing conditions inhibits crystallisation into zincian malachite or aurichalcite. The catalyst exhibits better performance for methanol synthesis and low temperature water-gas shift (LTS) reaction than a zincian malachite derived catalyst. It is suggested that alumina may not need to be added as a stabiliser. Alkali metals, which are known to act as catalyst poisons, are excluded from the synthesis procedure which is thought to account for the improved performance.

Harvesting Renewable Energy for Carbon Dioxide Catalysis

A. Navarrete, G. Centi, A. Bogaerts, Á. Martín, A. York and G. D. Stefanidis, *Energy Technol.*, 2017, **5**, (6), 796

Renewable energy can be used to transform carbon dioxide into commodities (CO₂ valorisation). Technological advances in the field are reviewed along with socioeconomic implications and the chemical basis of the transformation. Use of microwaves, plasmas and light to activate CO₂ are introduced and their fundamental phenomena discussed. The present state-of-the-art has inherent limitations. To solve these, the current catalytic concepts will need to be redesigned and a new conceptual approach for an energy-harvesting device is proposed. The future challenges in efficient conversion of CO₂ using renewable energy sources are described.