

Johnson Matthey Highlights

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

A Stochastic Approach to Model Chemical Looping Combustion

M. A. Schnellmann, G. Williams and J. S. Dennis, *Powder Technol.*, 2020, **365**, 39

Using two coupled fluidised-bed reactors, a stochastic model for reactor-regenerator systems was established. As a result the stochastic model was able to achieve the simulation of the circulating fluidised bed with acceptable precision. This model had been used before to comprehend how sensitive a chemical looping combustion (CLC) process is when other factors, for example the nature of gas-solid reactions, are included. To show the stochastic model has value for simulation and optimisation formations of CLC it is applied here with methane fuel gas in a laboratory-scale circulating fluidised bed.

ZSM-5 Additive Deactivation with Nickel and Vanadium Metals in the Fluid Catalytic Cracking (FCC) Process

A. A. Gusev, A. C. Psarras, K. S. Triantafyllidis, A. A. Lappas, P. A. Diddams and I. A. Vasalos, *Ind. Eng. Chem. Res.*, 2020, **59**, (6), 2631

This article explores properties of ZSM-5 additives and the role of nickel and vanadium in fluid catalytic cracking (FCC). Loadings of 4000 ppm and 12,000 ppm nickel and vanadium were found. There was deactivation of ZSM-5 in a cyclic deactivation unit and vacuum gas oil (VGO) reacted with nickel and vanadium naphthenates when cracking-regeneration reactions were undertaken. There was an even distribution of nickel across a particle where characterisation of deactivated ZSM-5 additives by nitrogen physisorption, SEM and pyridine FTIR techniques were used. The disparity was small in the Brønsted acidity, but when nickel and vanadium were added there was a rise in Lewis acidity. Further tests were carried out with VGO and where butylene increased,

propylene selectivity had a decrease in response to the metals.

$\text{Ga}_{2.52}\text{V}_{2.48}\text{O}_{7.33}(\text{OH})_{0.67}$, A Synthetic Member of the Nolanite/Akdalaite-Type Family of Oxyhydroxides Containing Trivalent Vanadium

D. S. Cook, M. R. Lees, J. M. Fisher, D. Thompsett and R. I. Walton, *J. Solid State Chem.*, 2020, **288**, 121396

Powder neutron diffraction shows oxyhydroxide $\text{Ga}_{2.52}\text{V}_{2.48}\text{O}_{7.33}(\text{OH})_{0.67}$ prepared by reaction between gallium metal and Na_3VO_4 in a 1:1 monoethanolamine:water mixture at 240°C demonstrates the material is isostructural with nolanite and akdalaite (**Figure 1**). Rietveld refinement was undertaken against the data showing all vanadium is octahedrally coordinated. Vanadium's oxidation state is close to V^{3+} when vanadium K-edge XANES spectroscopy is used. There is dehydration around 300°C (oxide $\text{Ga}_{2.52}\text{V}_{2.48}\text{O}_8$ is produced and has a larger amount of V^{4+}) followed by decomposition at 500°C. While both materials seem to follow the Curie-Weiss law at high temperatures, this is not so at low temperature. No reducing gas atmospheres are required in the preparation of V(III) oxides.

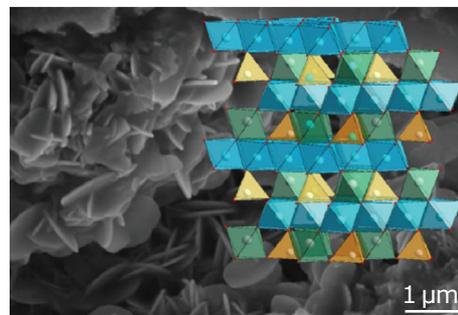


Fig. 1. Reprinted from D. S. Cook *et al.*, *J. Solid State Chem.*, 2020, **288**, 121396, Copyright (2020), with permission from Elsevier

Hierarchical ZSM-5 Catalysts: The Effect of Different Intracrystalline Pore Dimensions on Catalyst Deactivation Behaviour in the MTO Reaction

T. Weissenberger, A. G. F. Machoke, J. Bauer, R. Dotzel, J. L. Casci, M. Hartmann and W. Schwieger, *ChemCatChem*, 2020, **12**, (9), 2461

ZSM-5 zeolites used as methanol-to-olefins (MTO) catalysts were studied to determine the effect of intracrystalline pore systems in different combinations. Intracrystalline mesopores, intracrystalline macropores and a novel ZSM-5 type zeolite with both intracrystalline meso and macropores were used. There was a prolonged catalyst lifetime with the hierarchical catalysts unlike microporous only ZSM-5 catalyst. Using the intracrystalline mesopores and intracrystalline macropores as catalysts resulted in the ZSM-5 catalyst lasting up to three times longer. There were a number of important outcomes which were also noted including how mesopores and macropores effect catalyst deactivation. Overall, the study demonstrates intracrystalline macropores (alone or in combination with mesopores) significantly enhance the ZSM-5 catalytic performance in the MTO reaction.

Accelerating Pharmaceutical Development via Metal-Mediated Bond Formation

C. J. Borths and S. D. Walker, *Israel J. Chem.*, 2020, **60**, (3–4), 340

This article presents work being undertaken related to progress with metal-mediated carbon-carbon and carbon-heteroatom bond forming processes. The viewpoint of a current drug portfolio is used. Several case studies are discussed from the authors' laboratories looking at synthetic challenges plus prospects offered by pharmaceutically pertinent platforms. In several instances, available synthetic methods are challenged by target structures. This drives development permitting the acceleration of technology for drug development. There is also a discussion about metal-mediated processes at large scale.

Facile Synthesis of Precious-Metal Single-Site Catalysts Using Organic Solvents

X. Sun, S. R. Dawson, T. E. Parmentier, G. Malta, T. E. Davies, Q. He, L. Lu, D. J. Morgan, N. Carthey, P. Johnston, S. A. Kondrat, S. J. Freakley, C. J. Kiely and G. J. Hutchings, *Nature Chem.*, 2020, **12**, (6), 560

In many catalytic reactions, high activity and selectivity can be demonstrated by single-site catalysts. Creation of low metal loadings or a variety of metal species can be achieved by impregnation, for example, from strongly oxidising aqueous solutions. This study shows an atomic distribution of cationic metal species is achieved

with an impregnation of metal precursors onto activated carbon from a low boiling point solvent. Single-site gold, palladium, ruthenium and platinum catalysts supported on carbon were prepared in a facile method. In addition, it is shown that a single-site gold on carbon catalyst for acetylene hydrochlorination can be produced by this method.

Efficient and Selective Solvent-Free Homogeneous Hydrogenation of Aldehydes Under Mild Reaction Conditions Using [RuCl₂(dppb)(ampy)]

A. Zanotti-Gerosa, T. Angelini and S. Roseblade, *Tetrahedron Lett.*, 2020, **61**, (13), 151677

Using commercial grade aldehydes, effective, solvent-free homogeneous hydrogenation of aldehydes was undertaken with catalysts [RuCl₂(dppb)(ampy)] and [RuCl₂(dppf)(ampy)]. This gave high conversion to the related alcohols using molar catalyst loadings of 10,000/1–50,000/1. Aldehydes can be reduced preventing byproducts being formed with the minimum of waste which has led to a solvent-free protocol being established. This gives a straightforward hydrogenation technique for reduction of aldehydes to alcohols and commercial grade aldehydes require no further purification.

Innovation in Fischer-Tropsch: Developing Fundamental Understanding to Support Commercial Opportunities

M. Peacock, J. Paterson, L. Reed, S. Davies, S. Carter, A. Coe and J. Clarkson, *Top. Catal.*, 2020, **63**, (3–4), 328

The BP-Johnson Matthey proprietary Fischer-Tropsch technology and advanced CANS™ reactor and catalyst system are detailed. It provides improved heat transfer, reduced pressure drop and higher productivity and subsequently less financial expenditure. A clear understanding of how catalysts behave is crucial to finding a catalyst stable during its use and life. This report presents a study on catalyst activation on different catalyst supports and combines *in situ* techniques and reactor testing. Logical and systematic catalyst programmes are crucial for their development and are discussed in the results. Also, catalyst understanding, optimisation and development in combination with the novel CANS™ reactor design can maximise potential.

Cu/M:ZnO (M = Mg, Al, Cu) Colloidal Nanocatalysts for the Solution Hydrogenation of Carbon Dioxide to Methanol

A. H. M. Leung, A. García-Trenco, A. Phanopoulos, A. Regoutz, M. E. Schuster, S. D. Pike, M. S. P. Shaffer and C. K. Williams, *J. Mater. Chem. A*, 2020, **8**, (22), 11282

A synthesis is undertaken using controlled hydrolysis of a mixture of organometallic precursors

for doped-ZnO NPs capped with dioctylphosphinate ligands. Following substitutional doping and after hydrolysis, colloidal nanoparticles (2–3 nm) were characterised. Doped-ZnO nanoparticles and colloidal Cu(0) nanoparticles in solution were applied for hydrogenation catalysis of CO₂ to methanol in a liquid-phase continuous flow stirred tank reactor under the following conditions: 210°C, 50 bar, CO₂:H₂ = 1:3, 150 ml min⁻¹, mesitylene, 20 h. Higher rates are displayed for all catalyst systems with respect to methanol production compared to a benchmark catalyst. There is better stability. There was around double the activity for Al(III)-doped nanocatalyst. Mg(II) doping outperforms the benchmark catalyst but was worse compared to undoped ZnO. There is an implication that Al(III) migrates to the catalyst surface, and is proposed to enable stabilisation of the catalytic ZnO/Cu interfaces.

[N-Functionalised Imidazoles as Stabilisers for Metal Nanoparticles in Catalysis and Anion Binding](#)

C. J. Serpell, J. Cookson and P. D. Beer, *ChemistryOpen*, 2020, **9**, (6), 683

The physicochemical properties of metal NPs are discrete from bulk and molecular metal species. Consequently, this delivers opportunities in areas like catalysis and sensing, for example. The surface of the NPs usually need to be protected to hamper aggregation. However, access to the surface can also be blocked by these coatings preventing the ability to benefit from their uncommon properties. The article shows that palladium, platinum, gold and silver NPs can be stabilised by alkyl imidazoles. It also outlines the limits of their synthesis. Proof-of-principle in catalysis and anion binding is established showing that the ligands deliver a level of surface protection.

[In Situ K-edge X-ray Absorption Spectroscopy of the Ligand Environment of Single-Site Au/C Catalysts During Acetylene Hydrochlorination](#)

G. Malta, S. A. Kondrat, S. J. Freakley, D. J. Morgan, E. K. Gibson, P. P. Wells, M. Aramini, D. Gianolio, P. B. J. Thompson, P. Johnston and G. J. Hutchings,

Chem. Sci., 2020, **11**, (27), 7040

The environmental impact of acetylene hydrochlorination was substantially reduced by replacing HgCl₂/C with Au/C as a catalyst. Atomically dispersed cationic gold species are the catalytically active site. There have been limited studies which look at the ligand environment around the metal centre. This study uses K-edge soft XAS. Three separate chlorine species are identified and how they evolve in the reaction is demonstrated. Au–S interactions are established in catalysts prepared using thiosulfate precursors. The catalysts display evidence of high stability towards reduction to inactive metal NPs. Gas switching experiments made clear this stability. C₂H₂ on its own did not particularly change the gold electronic structure and the thiosulfate catalyst was not deactivated.

[Optimization of Biomass Pyrolysis Vapor Upgrading Using a Laminar Entrained-Flow Reactor System](#)

B. Peterson, C. Engtrakul, T. J. Evans, K. Iisa, M. J. Watson, M. W. Jarvis, D. J. Robichaud, C. Mukarakate and M. R. Nimlos, *Energy Fuels*, 2020, **34**, (5), 6030

To obtain understanding of commercial scale *ex situ* catalytic fast-pyrolysis (CFP) a customised bench-scale continuous-flow catalytic fast-pyrolysis CFP reactor system was built. The study successfully carried out CFP of pine over two commercial zeolite catalysts. The transmission of pyrolysis vapours to the vapour-phase upgrader was optimised to limit secondary thermal cracking and preserve carbon in the *ex situ* CFP process. Products attained were comparable to those from fixed bed and fluidised bed reactor systems and entrained-flow riser reactor systems. Experiments that duplicated the process provided a good average mass balance closure and comparable trends in deactivation of catalyst were seen in the laminar entrained-flow reactor system. There was a decreasing catalyst-to-biomass ratio. Optimised conditions suggest a feasible option for CFP of pine. For the two catalysts tested, minor variances were detected.