

Johnson Matthey Highlights

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

NON-PEER REVIEWED FEATURE

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Integration of Multi-Scale Porosimetry and Multi-Modal Imaging in the Study of Structure-Transport Relationships in Porous Catalyst Pellets

S. Mousa, V. Novak, R. S. Fletcher, M. Garcia, N. Macleod, M. Corfield and S. P. Rigby, *Chem. Eng. J.*, 2023, **452**, 139122

Batches of methanol synthesis catalyst pellets, made from various feed types, were characterised using multiscale porosimetry data and multi-modal imaging. This combined approach led to improvements in mutual interpretation. A simple random pore-bond network was used to model the impact on mass transfer of controlled modifications to the void space. Percolation analysis of overcondensation data was used to generate the characteristic parameters for the model. The method revealed the impact of different pellet fabrication parameters on tortuosity and the differential significance of certain sets of pores on mass transfer.

Computational Investigation of α -SiO₂ Surfaces as a Support for Pd

C. J. Lombard, C. G. C. E. van Sittert, J. N. Mugo, C. Perry and D. J. Willock, *Phys. Chem. Chem. Phys.*, 2023, **25**, (8), 6121

Dispersion-corrected DFT was used to study the interaction between palladium and periodic models of SiO₂ surfaces (α -SiO₂ (001), (100) and (101)). The modelled surfaces contained isolated siloxane and silanol functional groups. The authors estimated the affinity of the surfaces towards the adsorption of palladium atoms. The model was used to calculate the geometries of the Pd₁/ α -SiO₂ (*hkl*) adsorption site on each surface and to characterise the surface energies of the α -SiO₂ (*hkl*) surfaces. Pd₁(g) was predicted to

show a preference for adsorption near strained four-membered siloxane rings or on a vicinal silanol group of α -SiO₂ (101).

Recognizing the Best Catalyst for a Reaction

A. Lazaridou, L. R. Smith, S. Pattisson, N. F. Dummer, J. J. Smit, P. Johnston and G. J. Hutchings, *Nat. Rev. Chem.*, 2023, **7**, (4), 287

Heterogeneous catalysis provides access to materials which impact the wellbeing of society. Therefore, improvements to catalysts are constantly needed. An issue with this is that new catalysts are often assessed under different conditions which makes determining the best catalyst difficult. To combat this, the authors used a data set based on all reactions under kinetic control to determine a set of key performance indicators (KPIs). The KPIs were normalised and plots of the normalised KPIs were used to highlight the best catalyst. This was achieved using two case studies: acetylene hydrochlorination and selective oxidation of methane to methanol.

Co₃O₄/TiO₂ Catalysts Studied *in situ* During the Preferential Oxidation of Carbon Monoxide: The Effect of Different TiO₂ Polymorphs

T. M. Nyathi, M. I. Fadlalla, N. Fischer, A. P. E. York, E. J. Olivier, E. K. Gibson, P. P. Wells and M. Claeys, *Catal. Sci. Technol.*, 2023, **13**, (7), 2038

An incipient wetness impregnation technique was used to support Co₃O₄ nanoparticles on different TiO₂ polymorphs. The resulting Co₃O₄/TiO₂ catalysts were characterised *in situ* using magnetometry and PXRD. The best catalytic performance was observed when Co₃O₄ nanoparticles were supported on P25, with 72.7% carbon monoxide conversion to CO₂ at 200°C and a 91.9% degree of reduction (DoR) of Co₃O₄ to Co⁰ at 450°C. A DoR of 85.9% was seen for the rutile-support catalyst under reaction conditions. In the rutile- and P25-supported catalysts, unwanted CH₄ was formed over the Co⁰. This was

not observed for anatase-supported catalysts. The study reveals the impact of various TiO₂ polymorphs on the crystal phase and chemical transformations of Co₃O₄.

Catalytic, Z-Selective, Semi-Hydrogenation of Alkynes with a Zinc–Anilide Complex

G. Baker, A. White, I. Casely, D. Grainger and M. Crimmin, *ChemRxiv*, 2022, 16 pp

The authors report on the reversible activation of H₂ with a molecular zinc anilide complex which was investigated through DFT calculations and stoichiometric experiments. The results demonstrate that H₂ activation occurred with addition across the zinc–nitrogen bond *via* a four-membered transition state. At modest temperatures, the resulting zinc hydride complex was observed to be effective for the hydrozincation of C=C bonds. The hydrozincation of alkynes was faster than the equivalent alkene substrates as shown through competition experiments. The results from this study were applied to create a novel catalytic system for the semi-hydrogenation of alkynes.

Interfacial Chemistry in the Electrocatalytic Hydrogenation of CO₂ over C-Supported Cu-Based Systems

D. Gianolio, M. D. Higham, M. G. Quesne, M. Aramini, R. Xu, A. I. Large, G. Held, J.-J. Velasco-Vélez, M. Haevecker, A. Knop-Gericke, C. Genovese, C. Ampelli, M. E. Schuster, S. Perathoner, G. Centi, C. R. A. Catlow and R. Arrigo, *ACS Catal.*, 2023, **13**, (9), 5876

Plane-wave DFT simulations and *operando* X-ray spectroscopic techniques were used to explain the enhanced activities of zinc-containing copper nanostructured electrocatalysts in the electrocatalytic CO₂ hydrogenation reaction. Zinc was shown to alloy with copper in the bulk of the nanoparticles with no metallic zinc segregated. Several surface Cu(I) ligated species were identified which responded to the potential for CO₂ hydrogenation. The validity of this mechanism was confirmed but the performance was shown to decline after successive applied cathodic potentials, until the hydrogen evolution reaction becomes the

main reaction pathway. DFT simulations suggest that Cu–Zn–O neighbouring atoms can activate CO₂ and Cu–Cu sites supply hydrogen atoms for the hydrogenation reaction.

Transient CO Oxidation as a Versatile Technique to Investigate Cu²⁺ Titration, Speciation and Sites Hydrolysis on Cu–CHA Catalysts: The Cu Loading Effect

U. Iacobone, I. Nova, E. Tronconi, R. Villamaina, M. P. Ruggeri, J. Collier and D. Thompsett, *Top. Catal.*, 2023, *in press*

In this study, a dry transient carbon monoxide oxidation protocol with pre-stored NH₃ was applied to a group of Cu–CHA catalysts with variable copper loading. Investigation found that increasing the copper content had a positive impact on CO₂ production. The maximum carbon monoxide conversion was predicted through analysis of the integral CO₂ production. Further investigation showed asymptotic titration of the total catalyst Cu²⁺ contents in the presence of water. This work demonstrated the effectiveness and versatility of the carbon monoxide oxidation protocol as a multipurpose technique to study Cu²⁺ ions in Cu–CHA catalysts.

Perspectives on Current and Future Iridium Demand and Iridium Oxide Catalysts for PEM Water Electrolysis

M. Clapp, C. M. Zalitis and M. Ryan, *Catal. Today*, 2023, **420**, 114140

The future iridium demand of the global PEMWE sector was investigated and the role of different catalyst strategies for the improvement of iridium utilisation in the anode catalyst were examined. Modelling demonstrated that iridium utilisation must significantly improve by 2050 to prevent iridium supply limiting the capacity expansion. In addition, the installed capacity of iridium in 2050 could increase by ~2.7 times if closed-loop iridium recycling is realised by 2035. The authors predict that if these two conditions are achieved, global PEMWE capacity could realistically reach 1.3 TW by 2050 while using only 20% of annual global primary iridium supply (**Figure 1**).

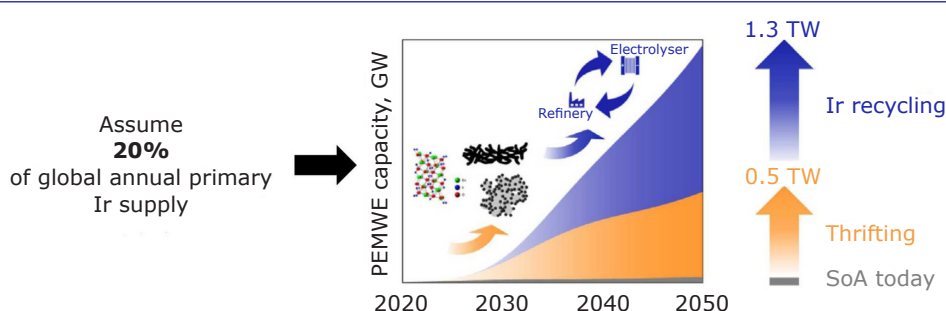


Fig. 1. Global PEMWE capacity over time. Reprinted from M. Clapp *et al.*, *Catal. Today*, 2023, **420**, 114140 under an Attribution-NonCommercial-NoDerivatives 4.0 International (CC BY-NC-ND 4.0) License

Towards Improved Conversion of Wet Waste to Jet Fuel with Atomic Layer Deposition-Coated Hydrodeoxygenation Catalysts

W. Wilson McNeary, J. H. Miller, S. A. Tacey, J. Travis, G. D. Lahti, M. B. Griffin, K. L. Jungjohann, G. Teeter, T. Eralp Erden, C. A. Farberow, L. Tuxworth, M. J. Watson, A. A. Dameron and D. R. Vardon, *Chem. Eng. J.*, 2023, **467**, 143268

The commercialisation of wet waste-derived volatile fatty acid conversion into jet fuel-range hydrocarbons is threatened by the moderate alkane selectivity of platinum-based hydrodeoxygenation catalysts and high costs. With the aim of addressing this, ALD was utilised to apply TiO₂ overcoats to Pt/Al₂O₃ catalysts. The new interface sites that this generated demonstrated a site time yield of the desirable *n*-alkane product eight times higher than an uncoated catalyst. Further calculations showed that under reducing conditions, oxygen vacancies were created at the platinum-TiO₂ interface for the ALD-coated catalyst. This led to increased selectivity and new Ti³⁺ acid sites near the active metal. Results demonstrate that the utility of precious-metal catalysts can be maximised using TiO₂ ALD.

Non-Carbon Greenhouse Gas Emissions for Hybrid Electric Vehicles: Three-Way Catalyst Nitrous Oxide and Ammonia Trade-Off

G. Brinklów, J. M. Herreros, S. Zeraati Rezaei, O. Doustdar, A. Tsolakis, A. Kolpin and P. Millington, *Int. J. Environ. Sci. Technol.*, 2023, *in press*

The three-way catalyst performance of a gasoline direct injection engine working under hybrid vehicle operation conditions was investigated. The abatement of both regulated and unregulated emissions was considered. Tailpipe NH₃ emissions were observed when the engine started while three-way catalyst temperatures were above 350°C. When the catalyst temperatures were below 150°C and the engine was started, N₂O and tailpipe regulated emissions increased. This was explained due to the selectivity of NO to form NH₃ at higher temperatures and N₂O at lower temperatures. A trade-off between regulated emissions (NH₃ and

N₂O) was achieved by starting the engine when the three-way catalyst was within a targeted temperature range.

Simulating Catalytic Reaction and Soot Oxidation in Coated Particulate Filters: A Simplified Modelling Framework Including Diffusion Effects

T. C. Watling, *Emiss. Control Sci. Technol.*, 2023, **9**, (2), 93

The author developed a simplified method for modelling catalysed particulate filters. The model incorporated the convection of gas through the particulate filter wall and soot cake from the inlet to the outlet channel, whilst avoiding the need to discretise in the through-wall direction. Even with the simplifications, the model revealed plausible predictions for soot oxidation and for the conversion of gaseous components. The model also included diffusion along the same axis. Diffusion through the wall was shown to be essential for NO₂ generated on the catalyst to be able to oxidise soot, however it had a smaller effect on the conversion of gaseous components.

Ditopic Extractants to Separate Palladium(II) and Platinum(IV) Chloridometalates via Inner or Outer Sphere Binding

A. M. Wilson, R. A. Grant, R. J. Gordon, J. B. Love, C. A. Morrison, K. J. Macruary, G. S. Nichol and P. A. Tasker, *Solvent Extr. Ion Exch.*, 2023, **41**, (4), 401

The authors were able to recover and extract palladium and platinum from acidic chloride solutions using a single ditopic extractant (**L**). This was achieved by utilising differences in the coordination chemistries of Pt(IV) and Pd(II). For instance: the distinctions in kinetic stability of the outer-sphere assemblies [(**LH**)₂·PtCl₆] of Pt(IV) and the inner sphere complexes [Pd(**L**)₂Cl₂] of Pd(II); the dependence of rates of ligand exchange in the inner sphere on the oxidation state and coordination number; and dependence of the formation of outer-sphere complexes/assemblies of chloridometalates on their charge:radius ratios. The investigation demonstrates proof of concept for the use of ditopic reagents in platinum and palladium extraction and separation.