

Johnson Matthey Highlights

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

NON-PEER REVIEWED FEATURE

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[Non-Kinetic Phenomena in Thermal Analysis Data; Computational Fluid Dynamics Reactor Studies](#)

R. L. Gibson, M. J. H. Simmons, E. H. Stitt, L. Liu and R. W. Gallen, *Chem. Eng. J.*, 2021, **426**, 130774

A characterisation method for the transport phenomena happening in thermal analysis reactors was developed using computational fluid dynamics. Comparison of different equipment configurations was possible using this method to identify the most suitable for obtaining intrinsic data. From two broad categories (pan-style and tubular reactors) four equipment configurations are compared. There are heat and mass transport issues in pan-style and non-uniform diameter tubular reactor configurations. These should be avoided if extraction of kinetic parameters is the aim. In kinetic experimentation uniform diameter tubular reactors are suitable. However, checks should be conducted using the dimensionless analysis that this article describes.

[Support and Gas Environment Effects on the Preferential Oxidation of Carbon Monoxide over Co₃O₄ Catalysts Studied *In Situ*](#)

T. M. Nyathi, M. I. Fadlalla, N. Fischer, A. P. E. York, E. J. Olivier, E. K. Gibson, P. P. Wells and M. Claeys, *Appl. Catal. B: Environ.*, 2021, **297**, 120450

This study was conducted to look at the effect of different supports (ceria, zirconia, silicon carbide, silica and alumina) on phase stability of Co₃O₄ nanoparticles and the catalytic performance during the preferential oxidation of carbon monoxide (CO-PrOx) under different temperatures and hydrogen-rich gas environments. It concludes that, possibly *via* the Mars-van Krevelen mechanism, weak nanoparticle-support interactions (as in

Co₃O₄/zirconia) favour high carbon monoxide oxidation activity. However, Co⁰ and methane formation are minimised by stronger interactions (as in Co₃O₄/alumina). Consequently, this study shows the bifunctional role required of supports used in CO-PrOx, for example, to improve the phase stability of Co₃O₄ and enhance catalytic performance.

[The H₂O Effect on Cu Speciation in Cu-CHA-Catalysts for NH₃-SCR Probed by NH₃ Titration](#)

R. Villamaina, F. Gramigni, U. Iacobone, S. Liu, I. Nova, E. Tronconi, M. P. Ruggeri, J. Collier, A. P. E. York and D. Thompsett, *Catalysts*, 2021, **11**, (7), 759

This article considers the effect of water on ammonia adsorption over copper-chabazite SCR catalysts. Under dry and wet conditions, samples characterised by different SAR (silica:alumina) ratios and copper loadings were studied. Of all the tested catalysts, water adversely affects ammonia adsorption on Lewis acid sites as shown by the decreased ammonia desorption at low temperature during TPD. The ammonia:copper ratio fell in the range of 3–4 or 1–2 in dry conditions, in line with the formation of different ammonia-solvated copper species. Contrarily, when water was fed to the system the ammonia:copper ratio was always close to 3 (or 1), and Brønsted acidity slightly increased.

[Effect of RF Magnetron Sputtering Parameters on the Optimization of the Discharge Capacity of Ternary Lithium Oxide Thin Films](#)

D. A. S. Lopez, L. G. Chagas, A. D. Batista, M. G. D. Guaita, L. H. C. Amorin, P. R. C. da Silva, G. Yamanishi, D. A. M. Zaia, H. de Santana and A. Urbano, *J. Mater. Sci.: Mater. Electron.*, 2021, **32**, (13), 17462

This article investigates materials created of ternary lithiated oxide compounds as an alternative to reduce costs and toxicity of lithium-ion battery

cathodes. It researches the effect of sputtering deposition parameters on the charge capacity of ternary compound material thin films analysing the impact small changes in crystalline and morphological structures have on charge capacity at low cell potentials. Without additional thermal treatments, high discharge capacity was obtained favouring the manufacture of films over polymeric substrates in future electronic applications.

Monitoring Dynamics of Defects and Single Fe Atoms in N-Functionalized Few-Layer Graphene by *in situ* Temperature Programmed Scanning Transmission Electron Microscopy

R. Arrigo, T. Sasaki, J. Callison, D. Gianolio and M. E. Schuster, *J. Energy Chem.*, 2022, **64**, 520

This study seeks to broaden understanding of the pathway of formation of iron species during top-down synthesis of dispersed iron on nitrogen-functionalised few layer graphene. The study uses XAS and shows high mobility of peripheral iron atoms. Within the results, the significance is that single iron atoms in graphene are highly mobile. This means a structural description of the electroactive sites is insufficient and more complex species might be more relevant. This is especially the case of multielectron transfer reactions and the results provide the experimental evidence of the formation of these polynuclear iron–nitrogen sites and their structural characteristics.

Preparation of Neutral *trans-cis* [Ru(O₂CR)₂P₂(NN)], Cationic [Ru(O₂CR)P₂(NN)](O₂CR) and Pincer [Ru(O₂CR)(CNN)P₂] (P = PPh₃, P₂ = diphosphine) Carboxylate Complexes and their Application in the Catalytic Carbonyl Compounds Reduction

S. Baldino, S. Giboulot, D. Lovison, H. G. Nedden, A. Pöthig, A. Zanotti-Gerosa, D. Zuccaccia, M. Ballico and W. Baratta, *Organometallics*, 2021, **40**, (8), 1086

This article describes the preparation of a class of carboxylate ruthenium complexes containing triphenylphosphine and diphosphines. Through straightforward syntheses from [Ru(κ^2 -OCOR)₂(PPh₃)₂], a diphosphine and NN ligands, neutral *trans* and *cis* complexes of the formula [Ru(OCOR)₂P₂(NN)] and the cationic complexes [Ru(O₂CR)P₂(NN)](O₂CR) have been isolated. The described complexes show good catalytic activity in the transfer hydrogenation and hydrogenation of carbonyl compounds. This protocol is being extended to the preparation of ruthenium carboxylate complexes with NN and CNN pincer ligands for use in catalytic organic transformations.

Modelling of Mass Transfer Resistances in Non-Uniformly Washcoated Monolith Reactors

M. Walander, J. Sjöblom, D. Creaser, B. Agri, N. Löfgren, S. Tamm and J. Edvardsson, *Emiss.*

Control Sci. Technol., 2021, **7**, (2), 153

In this study, the authors developed a novel way to account for local material properties (such as cracks or washcoat thickness) in a washcoated monolith reactor. A preexisting 1+1D modelling framework was utilised, and the washcoat was divided into various tangential segments. SEM and intelligent gravimetric analysis techniques were used to determine local effective diffusivity as an input for each segment. Nitric oxide light-off simulations were used to assess the new model against the original 1+1D model. Due to the parallelisable character of the new model, both models had a comparable simulation time. The new model was also able to predict increased conversion at elevated temperatures.

Design Parameters for Ionic Liquid–Molecular Solvent Blend Electrolytes to Enable Stable Li Metal Cycling Within Li–O₂ Batteries

A. R. Neale, R. Sharpe, S. R. Yeandel, C.-H. Yen, K. V. Luzyanin, P. Goddard, E. A. Petrucco and L. J. Hardwick, *Adv. Funct. Mater.*, 2021, **31**, (27), 2010627

DMSO, a common electrolyte used to support lithium-oxygen cathode processes, is incompatible with lithium-metal. Therefore, ternary solutions based on salt, ionic liquid and solvent were investigated to determine the effect of tailoring formulations on the electrochemical stability and performance of DMSO at lithium-metal electrodes. The enhanced formulations demonstrated improved performance in lithium-oxygen full cells, stable lithium plating and stripping performances and Columbic efficiencies >94%. The continued importance of DMSO-Li⁺-cation interactions was highlighted through the simulation of local solvation environments, spectroscopic characterisation and characterisation of lithium surfaces. The authors suggest that non-volatile ionic liquid could be carefully added to tailor additional electrolyte properties in lithium-oxygen cells.

X-Ray Molecular Structure Characterization of a Hexamethylenetetramine Zinc(II) Porphyrin Complex, Catalytic Degradation Of Toluidine Blue Dye, Experimental and Statistical Studies of Adsorption Isotherms

J. Brahmi, S. Nasri, C. Briki, M. Guergueb, S. Najmudin, K. Aouadi, M. R. Sanderson, M. Winter, D. Cruickshank and H. Nasri, *J. Mol. Liq.*, 2021, **341**, 117394

The single crystal X-ray molecular structure of pentacoordinate zinc(II) porphyrin coordination compound [Zn(*meso*-tetrakis[(*para*-tetratrifluoromethylphenyl)]porphyrinato (TFMPP)) (hexamethylenetetramine (HMTA))] (complex (I)) was reported. Next, free base porphyrin H₂TFMPP and

the metallated zinc(II)-HMTA-porphyrin derivative (I) were used as adsorbents for toluidine blue (BT) dye. Adsorption of the BT dye was interpreted through advanced statistical models, such as the Langmuir model and the pseudo-second-order kinetic model. The adsorption of the BT pollutant on complex (I) and the free base porphyrin H₂TFMPP was shown to be possible, and spontaneous. Complex (I) was a suitable catalyst for the removal of BT dye in a 30% aqueous hydrogen peroxide solution.

Ostwald Ripening Microkinetic Simulation of Au Clusters on MgO(001)

S. Francis, A. Boucher, G. Jones and A. Roldan, *Appl. Surf. Sci.*, 2022, **572**, 151317

Microkinetic simulations and *ab initio* calculations were combined to study the growth and digestion mechanism on gold clusters supported on MgO(001). In the cases investigated, activation energies were below 1.05 eV. Due to the stability of pairing the unpaired electrons associated with the single gold atoms, an odd-even cluster trend was detected when ripening. Gold single atoms were observed on the surface of magnesia at temperatures <160 K. Above 160 K, the gold single atom diffused across the surface and attached to other clusters (**Figure 1**) or individual atoms. A more stable equilibrium was achieved at room temperature, where the cluster underwent ripening to create larger particles.

Investigation of Iridium, Ruthenium, Rhodium, and Palladium Binary Metal Oxide Solid Solution Thin Films for Implantable Neural Interfacing Applications

G. Taylor, J. Shallenberger, S. Tint, A. Fones, H. Hamilton, L. Yu, S. Amini and J. Hettinger, *Surf. Coatings Technol.*, 2021, **426**, 127803

DC reactive magnetron sputtering was employed to synthesise metal oxide solid solution thin films containing binary mixtures of ruthenium, iridium, palladium and rhodium. The microstructural and electrochemical characteristics of the binary metal oxides were compared to those of their single metal oxide endmembers. At a film thickness greater than 700 nm, the binary metal oxides demonstrated greater electrochemical performance than their single metal endmembers. The electrochemical enhancements observed can be partly attributed to higher oxidation states in the binary metal oxides, as shown by XPS analyses.

Pre-Combustion Gas Separation by ZIF-8-Polybenzimidazole Mixed Matrix Membranes in the Form of Hollow Fibres – Long-Term Experimental Study

A. Perea-Cachero, M. Etxeberria-Benavides, O. David, A. Deacon, T. Johnson, M. Malankowska, C. Téllez and J. Coronas, *R. Soc. Open Sci.*, 2021, **8**, (9), 210660

Polybenzimidazole (PBI) is a promising membrane polymer for the separation of the hydrogen/carbon dioxide pre-combustion gas mixture. In this study, PBI hollow fibres were prepared as mixed matrix membranes with MOF ZIF-8 as a filler, and hydrogen/carbon dioxide separation properties were continuously measured. Over approximately 51 days, operation conditions were examined at 200°C and the effects of membrane healing with poly(dimethylsiloxane) were investigated. The hydrogen permeance was in the 22–47 GPU range for all the membranes studied, which corresponds to 22–32 hydrogen/carbon dioxide selectivity values.

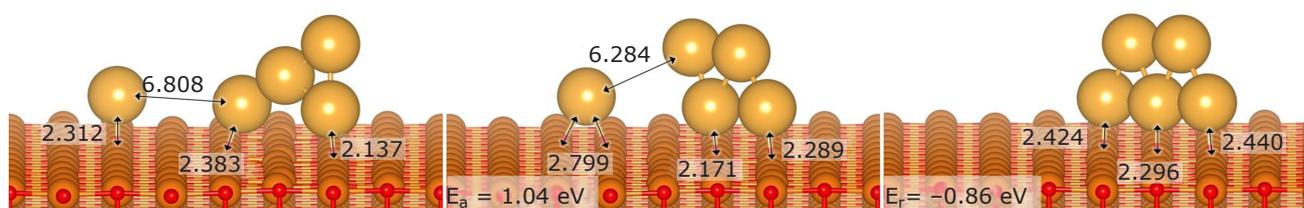


Fig. 1. Representation of a single atom attachment path to an Au₄ cluster leading to Au₅. Distances are represented in Angstroms between gold and the binding oxygen. The colour scheme is as follows: Orange = magnesium, red = oxygen and gold = gold. Reprinted under Creative Commons Attribution 4.0 International (CC BY 4.0).