JOHNSON MATTHEY
TECHNOLOGY REVIEW
www.technology.matthey.com

Johnson Matthey Highlights

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

Fast Synthesis of n-type Half-Heusler TiNiSn Thermoelectric Material

K. Chen, C. Nuttall, E. Stefanaki, K. Placha, R. Tuley, K. Simpson, J.-W. G. Bos and M. J. Reece, *Scr. Mater.*, 2021, **191**, 71

In the medium temperature range for thermoelectric applications the n-type half-Heusler TiNiSn is very promising. Unfortunately, there is a major barrier related to scaling up as several weeks annealing time is required for the synthesis of TiNiSn. A mixture of arc-melting, ball-milling and spark plasma sintering was used in this work to synthesise TiNiSn. High-purity, high-density and fine grains with diameters of up to 30 mm were obtained in the samples. To improve the thermoelectric properties of TiNiSn, copper was added which achieved, at 773 K, a maximum figure of merit of 0.6. The possibility of industrial scaling-up has been opened up by the fast and scalable synthesis of TiNiSn.

First Principle Studies on Lattice Thermal Conductivity and Thermoelectric Properties of $ScCu(S,Se,Te)_2$

E. Rugut, D. Joubert and G. Jones, *Mater. Today Commun.*, 2021, **26**, 101905

In this study, based on first principles, the aim is to consider scandium copper chalcogenides ($ScCuX_2$) to evaluate lattice thermal conductivity, transport properties, the thermoelectric figure of merit and structural stability. Evaluations include Debye temperatures plus transverse and longitudinal sound velocity in $ScCuX_2$ compounds along with phonon lifetimes, mean free paths and group velocities. Among the three ternary compounds in the findings, when the majority charge carriers are holes having a carrier concentration of 1019 cm^{-3}, $ScCuSe_2$ has the highest value of dimensionless figure of merit of 0.65 at high temperatures (1000 K).

Terahertz Pulsed Imaging as a New Method for Investigating the Liquid Transport Kinetics of *α*-Alumina Powder Compacts

M. Al-Sharabi, D. Markl, V. Vivacqua, P. Bawuah, N. MacLean, M. Bentley, A. P. E. York, M. Marigo, K. Huang and J. A. Zeitler, *Chem. Eng. Res. Des.*, 2021, **165**, 386

Terahertz pulsed imaging was used to investigate liquid transport kinetics of α-alumina powder compacts formed under different sintering conditions and compaction forces. There was an impact on the water ingress rate due to the surface properties and microstructure characteristics of the alumina compacts. It was shown that the mass transport characteristics were consistent with Darcy flow. The hydraulic radius was calculated based on the transport data.

Passivation of Co/Al_2O_3 Catalyst by Atomic Layer Deposition to Reduce Deactivation in the Fischer–Tropsch Synthesis

J. A. Díaz-López, J. Guilera, M. Biset-Peiró, D. Enache, G. Kelly and T. Andreu, *Catalysts*, 2021, **11**, (6), 732

The work undertaken looks to reduce deactivation rate during Fischer-Tropsch synthesis (FTS) through the possibility of passivating a Co/ γ-Al_2O_3 catalyst by atomic layer deposition (ALD). Different numbers of ALD cycles (3, 6 and 10) were used with three samples of the reference catalyst. The results showed a shell of the passivating agent (Al_2O_3) growing around the catalyst particles which did not affect the properties of passivated samples below 10 cycles though it hindered catalyst reduction. Catalytic tests at 50% and 60% CO conversion were conducted. The technical feasibility of this technique was proven in FTS as 3 to 6 ALD cycles reduced Co/γ-Al_2O_3 deactivation.

Monitoring the Process of Formation of ZnO from ZnO_2 using *in situ* Combined XRD/XAS Technique

T. Daley, K. B. Opuni, E. Raj, A. J. Dent, G. Cibin, T. I. Hyde and G. Sankar, *J. Phys. Condens. Matter*, 2021, **33**, (26), 264002

The thermal decomposition of zinc peroxide to zinc oxide is reported here. XAS and *in situ* combined XRD were used to conduct the study. From the data extracted comparison was made of XRD and XAS with TGA. This enabled the nature of the conversion of ZnO_2 to ZnO to be followed. Using a temperature range of 230–350ºC seems to show, prior to forming an ordered ZnO material, that a poor crystalline ZnO is formed. White line intensity decreases in the zinc K-edge XANES plus lower coordination numbers from analysis of the zinc K-edge data of ZnO heated at 500ºC, compared to bulk ZnO, suggests significant defects in the system for the ZnO produced.

Dense Pt Nanowire Electrocatalyst for Improved Fuel Cell Performance Using a Graphitic Carbon Nitride-Decorated Hierarchical Nanocarbon Support

B. Fang, L. Daniel, A. Bonakdarpour, R. Govindarajan, J. Sharman and D. P. Wilkinson, *Small*, 2021, **17**, (30), 2102288

Engineering supported-platinum nanowire (NW) electrocatalysts with a high platinum content for the cathode of hydrogen fuel cells is presented in this innovative strategy. This uses g-CN@MPC formed by the deposit of graphitic carbon nitride (g-CN) onto 3D multimodal porous carbon (MPC) as an electrocatalyst support. Improved performance was observed with the g-CN@MPC-supported high-content platinum catalysts in relation to their counterparts. These were MPC, VC and g-CN@VC-supported platinum NW catalysts. Also for the benchmark catalyst the conventional platinum nanoparticle catalyst (Pt(20 wt%)NPs/VC (Johnson Matthey)) was used. At a very low cathode catalyst loading (≈0.1 $mg_{Pt}\,cm^{-2}$), a high PEM fuel cell power/performance is demonstrated by the g-CN-tailored high-content platinum NW (≈60 wt%) electrocatalyst.

The Role of Chromium in Iron-Based High-Temperature Water-Gas Shift Catalysts under Industrial Conditions

M. I. Ariëns, V. Chlan, P. Novák, L. G. A. van de Water, A. I. Dugulan, E. Brück and E. J. M. Hensen, *Appl. Catal. B Environ.*, 2021, **297**, 120465

This study investigated chromium promotion of iron oxide based water-gas shift catalysts prepared *via* calcination/coprecipitation. The catalysts were aged for four days under realistic conditions. XRD and Mössbauer spectroscopy results demonstrated that chromium is incorporated in the calcined haematite (α-Fe_2O_3) precursor. Chromium doping was shown to affect the activation of α-Fe_2O_3. Increasing the chromium doping led to enhanced CO conversion and to an increased Fe^{3+}:Fe^{2+} ratio in octahedral sites of magnetite. Computational studies modelling the chromium and vacancy-doped magnetite structures supported the results of the Mössbauer spectra. The study concluded that the bulk structure of an *in situ* prepared chromium-doped high-temperature water-gas shift catalyst is best expressed as a partially oxidised chromium-doped magnetite phase.

Atomic Layer Deposition with TiO_2 for Enhanced Reactivity and Stability of Aromatic Hydrogenation Catalysts

W. W. McNeary, S. A. Tacey, G. D. Lahti, D. R. Conklin, K. A. Unocic, E. C. D. Tan, E. C. Wegener, T. E. Erden, S. Moulton, C. Gump, J. Burger, M. B. Griffin, C. A. Farberow, M. J. Watson, L. Tuxworth, K. M. Van Allsburg, A. A. Dameron, K. Buechler and D. R. Vardon, *ACS Catal.*, 2021, **11**, (14), 8538

ALD was used to apply an ultrathin coating of TiO_2 on a conventional supported palladium catalyst in a scalable powder coating process, with the aim of enhancing hydrogenation performance. The TiO_2-coated catalyst displayed significant gains in the conversion of multiple aromatic molecules, and such enhancements were maintained when the coating synthesis process was scaled from 3 g to 100 g. Computational modelling, XAS and XPS results attributed the activity enhancement to ensemble effects resulting from partial TiO_2 coverage of the palladium surface. Further investigation showed that the TiO_2 coating improved the catalyst's hydrothermal stability, tolerance toward sulfur impurities in the reactant stream and thermal stability.

Platinum Incorporation into Titanate Perovskites to Deliver Emergent Active and Stable Platinum Nanoparticles

M. Kothari, Y. Jeon, D. N. Miller, A. E. Pascui, J. Kilmartin, D. Wails, S. Ramos, A. Chadwick and J. T. S. Irvine, *Nat. Chem.*, 2021, **13**, (7), 677

A resilient catalyst was achieved using a perovskite system incorporating 0.5 wt% platinum into the support and its subsequent conversion through exsolution. Barium platinate, which is a thermally stable platinum oxide precursor, was utilised to preserve the platinum as an oxide throughout the solid-state synthesis. An equilibrated and uniform structure with active emergent platinum nanoparticles strongly embedded in the perovskite surface was attained by tailoring the procedure. In comparison to conventionally prepared platinum catalysts, the structure demonstrated greater stability and CO oxidation activity. Further investigations studied ammonia slip reactions, CO and NO oxidation and diesel oxidation catalysis.

Operando Neutron Scattering: Following Reactions in Real Time Using Neutrons

V. Skukauskas, E. L. B. Johnson Humphrey, I. Hitchcock, A. York, J. Kelleher, E. K. Gibson, D. J. Nelson and I. P. Silverwood, *Top. Catal.*, 2021, **64**, (9–12), 693

In this study, quasielastic neutron scattering was used to observe reaction progress in the complexation of $NiCl_2$ with 2,2′-bipyridine. A high-resolution engineering diffractometer was used to induce strain in the aluminosilicate framework, and thus observe water adsorption in chabazite with time resolution. The results from this work highlight the recent advances and future possibilities of using neutron probes for the observation of realistic catalytic reactions as they proceed.

Roles of the Basic Metals La, Ba, and Sr as Additives in Al_2O_3-Supported Pd-Based Three-Way Catalysts

Y. Jing, G. Wang, K. W. Ting, Z. Maeno, K. Oshima, S. Satokawa, S. Nagaoka, K. Shimizu and T. Toyao, *J. Catal.*, 2021, **400**, 387

A variety of spectroscopic and kinetic studies were conducted to investigate the roles of typical basic metal additives (barium, lanthanum and strontium) in palladium-based TWC systems. Metallic Pd^0 species on La/Al_2O_3 were electron-deficient, whereas those on Ba/Al_2O_3 and Sr/Al_2O_3 supports were more electron-rich compared to those on pristine Al_2O_3 (**Figure 1**). During NO reduction reactions, $Pd/La/Al_2O_3$ exhibited a lessened CO poisoning effect. Further studies using both powdered and monolithic catalysts showed that $Pd/Ba/Al_2O_3$ exhibited the highest activity for the oxidations of CO and C_3H_6, and $Pd/La/Al_2O_3$ promoted the catalytic reduction of NO most efficiently. The authors concluded that the optimal metal additive for a palladium-based TWC should be ascertained by the specific application.

Packing Simulations of Complex-Shaped Rigid Particles using FDEM: An Application to Catalyst Pellets

A. Farsi, J. Xiang, J.-P. Latham, M. Carlsson, H. Stitt and M. Marigo, *Powder Technol.*, 2021, **380**, 443

The effects of friction, geometric features and energy dissipation parameters on the bulk properties of rigid pellet packs were estimated by employing a new component of the combined finite-discrete element method (FDEM). The numerical simulations of packing of glass beads, trilobe pellets and cylindrical catalyst supports were confirmed to match the corresponding emergent bulk properties attained from X-ray CT scans. This study is the first to confirm the applicability of FDEM based methods to the simulation of this class of multi-body problems.

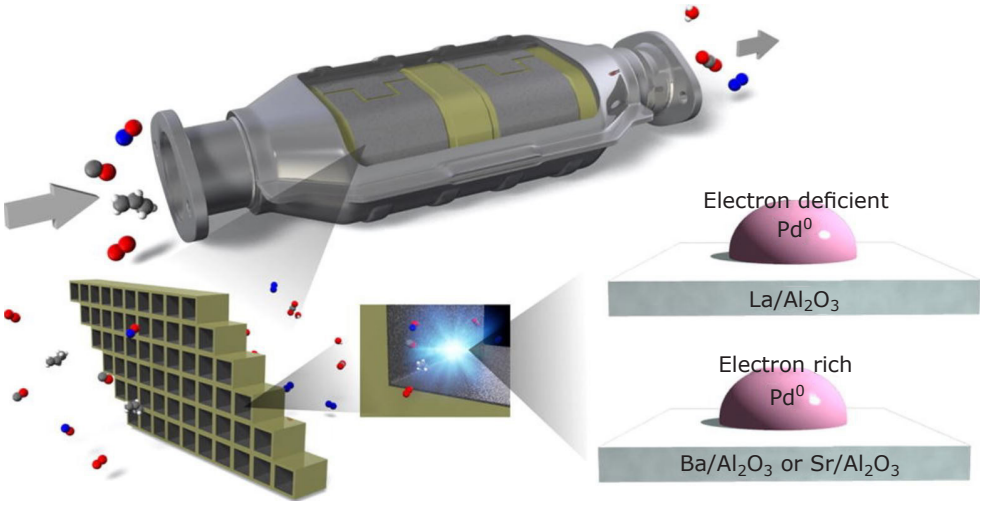

Fig. 1. Reprinted from Y. Jing *et al*., *J. Catal.*, 2021, **400**, 387, Copyright (2021), with permission from Elsevier