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Johnson Matthey Highlights

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

In Situ Surface Analysis of Palladium–Platinum Alloys in Methane Oxidation Conditions

A. I. Large, R. A. Bennett, T. Eralp-Erden and G. Held, *Faraday Discuss.*, 2022, **236**, 157

Temperature-programmed near-ambient pressure X-ray photoelectron spectroscopy was utilised under methane oxidation conditions to examine palladium and palladium-platinum foils. Results from the analysis demonstrated that the presence of water inhibits the oxidation of palladium in oxygen-poor environments. The addition of platinum hindered the oxidation of palladium further. This occurred across various reaction conditions, which meant that metallic palladium was preserved at higher temperatures. Under reaction conditions, bimetallic foils endured significant restructuring. Platinum showed a preference to migrate to the bulk under select conditions.

Effect of Oxygen Storage Materials on the Performance of Pt-based Three-Way Catalysts

G. Wang, Y. Jing, K. W. Ting, Z. Maeno, X. Zhang, S. Nagaoka, K. Shimizu and T. Toyao, *Catal. Sci. Technol.*, 2022, **12**, (11), 3534

Kinetic studies and spectroscopic observations were used to investigate the effect of oxygen storage materials (OSMs) on the three-way catalysis performance of platinum/OSMs. Platinum/OSM(66%CeO_2) exhibited the most stability among the three-way catalysts. The formation of nitrite species and their reactivity to carbon monoxide improved by increasing the ceria content in fresh platinum/OSMs. This also enhanced the resistance to carbon monoxide poisoning during NO–CO reactions. Both platinum and ceria species in platinum/OSMs were shown to be involved in NO–CO reactions through their redox cycles. XRD and XAS measurements highlighted that the aggregation of platinum particles and lattice contraction of CeO_2 in platinum/OSMs was the result of hydrothermal ageing treatment.

Comparison between the Thermal and Plasma (NTP) Assisted Palladium Catalyzed Oxidation of CH_4 using AC or Nanopulse Power Supply

F. De Rosa, C. Hardacre, W. G. Graham, G. McCullough, P. Millington, P. Hinde and A. Goguet, *Catal. Today*, 2022, **384**, 177

A palladium supported on alumina catalyst was used to investigate the combustion of methane using three different systems (thermocatalytic, plasma-catalyst and plasma). The potential presence of a synergistic effect between the plasma and the heterogeneous catalyst and the specific input energy were compared for each system. Specific input energy results demonstrated that the thermal process was more efficient than the plasma systems. A synergistic effect was not observed for the plasma systems when an AC power supply was used. A nanopulsed power supply was also investigated. By using a nanopulsed power supply, energy requirements in the heterogeneous and homogeneous configurations were reduced. High conversion was observed at energy levels where the thermocatalytic process with a commercial catalyst was not active.

Selection of Formal Baseline Correction Methods in Thermal Analysis

R. L. Gibson, M. J. H. Simmons, E. H. Stitt, L. Horsburgh and R. W. Gallen, *Chem. Eng. Technol.*, 2022, **45**, (2), 238

Baseline correction is a common and pivotal step when processing thermal analysis data. Different techniques can be used and these include the use of high-order polynomials and linear baselines. Only linear correction methods should be employed when considering a formal baseline correction (i.e. those without experimental or

physical justification). These methods are linear with extent of reaction, linear with time and linear with temperature. An *in silico* investigation was undertaken and results demonstrated that using the incorrect baseline correction had a significant impact on the parameters attained from kinetic modelling. The authors present four baseline correction methods with a mass spectrometry dataset. They concluded that Akaike weights should be used to inform the correction method selection.

Flow Behaviour of Zeolite Powders at High Process Temperatures

S. Z. Ajabshir, C. Gucuyener, V. Vivacqua, D. Gobby, H. Stitt, D. Barletta and M. Poletto, *Powder Technol.*, 2022, **409**, 117818

Two zeolite powders, T804 and Z302, were assessed in the range of 1–8 KPa for normal consolidation stresses at temperatures of 150ºC, 300ºC and 500ºC by an Anton Paar shear cell. Flow properties were evaluated and diverse flowability behaviour was observed for the two materials. A theoretical framework was developed to incorporate the different particle size distributions of Z302 and T804. This was used to clarify why the two powders had different consolidation changes and temperature behaviours. Different powder bulk densities were accounted for with an original analysis of flowability based on the calculation of a structural length.

Pathways to Sustainable Methanol Operations using Gas-Heated Reforming (GHR) Technologies

J. Mahabir, N. Samaroo, M. Janardhanan and K. Ward, *J. CO2 Util.*, 2022, **66**, 102302

The effectiveness of several innovative low carbon technologies in promoting sustainable methanol operations was investigated. This included ATR, SMR-CCS and GHR. GHR demonstrated a 17% increase in resource efficiency over the SMR and ATR processes and an 11% increase in energy efficiency. The GHR systems also achieved a 14–41% reduction in GHG emissions compared to SMR and ATR, when coupled with electrification and CCS. The GHR systems were also the most economical. The environmental and economic benefits observed make GHR systems the ideal candidates for future low carbon methanol operations.

Promoting Effect of Basic Metal Additives on DeNOx Reactions over Pt-Based Three-Way Catalysts

Y. Jing, G. Wang, S. Mine, J. Kawai, R. Toyoshima, H. Kondoh, X. Zhang, S. Nagaoka, K. Shimizu and T. Toyao, *J. Catal.*, 2022, **416**, 209

The effect of basic metal additives in $Pt/M/Al_2O_3$ (M = lanthanum, barium and strontium) on three-way catalytic reactions was investigated. Barium enhanced the catalytic activity of platinum-based catalysts more than lanthanum and strontium. Several *in situ*/*operando* spectroscopic experiments and kinetic studies were performed on $Pt/Ba/Al_2O_3$, the best performing catalyst. AP-XPS results showed that Pt^0 species loaded on Ba/Al_2O_3 were more electron-rich than those loaded on Al_2O_3 and this promoted NO dissociation into nitrogen and oxygen atoms. The effect of barium on the NO reduction reaction was intrinsically linked to the formation of intermediate surface NOx species and their reactivities toward reductant gases.

Lowering the Operating Temperature of Gold Acetylene Hydrochlorination Catalysts Using Oxidized Carbon Supports

S. Pattisson, S. R. Dawson, G. Malta, N. F. Dummer, L. R. Smith, A. Lazaridou, D. J. Morgan, S. J. Freakley, S. A. Kondrat, J. J. Smit, P. Johnston and G. J. Hutchings, *ACS Catal.*, 2022, **12**, (22), 14086

The authors investigated the impact of support surface oxygen on carbon-supported gold catalyst activity (**Figure 1**). The Hummers chemical oxidation method was carefully modified before the deposition of gold in order to attain variation in the surface oxygen content of carbon. In comparison to the standard nontreated carbon, all oxidised carbon-based catalysts demonstrated an activity increase at 200ºC. Light-off temperatures 30–50ºC lower than the standard catalyst were achieved by increasing oxygen and the relative concentration of C–O functionality. This work provides a basis for creating high activity acetylene hydrochlorination catalysts that can operate at lower temperatures.

Substituting Chromium in Iron-Based Catalysts for the High-Temperature Water–Gas Shift Reaction

M. I. Ariëns, L. G. A. van de Water, A. I. Dugulan, E. Brück and E. J. M. Hensen, *ACS Catal.*, 2022, **12**, (22), 13838

A one-step calcination/coprecipitation approach was used to prepare doped iron oxides and their WGS activity was evaluated under industrial conditions. Regardless of dopant, the activated catalysts mainly consisted of magnetite. Zinc and aluminium were shown to occupy octahedral and tetrahedral sites of magnetite in aged catalyst, whereas the other oxides preferentially substituted octahedral iron. Niobium- and indium-doped catalysts demonstrated

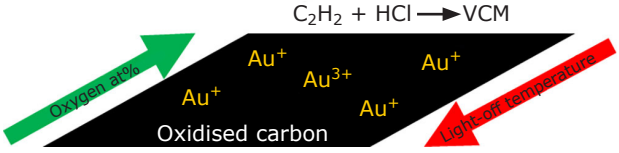

Fig. 1. Reprinted from S. Pattisson *et al.*, *ACS Catal.*, 2022, **12**, (22), 14086 under Creative Commons Attribution 4.0 International (CC BY 4.0)

distinct dopant metal oxide phases. In activated copper-codoped catalysts, copper was present as a separate phase, as shown by XPS analysis. The most promising promoter to substitute chromium in commercial high-temperature WGS catalysts was aluminium, due to its comparable carbon monoxide conversion.

Enhanced Photoacoustic Visualisation of Clinical Needles by Combining Interstitial and Extracorporeal Illumination of Elastomeric Nanocomposite Coatings

M. Shi, S. Bodian, S. J. West, S. Sathasivam, R. J. Gordon, P. Collier, T. Vercauteren, A. E. Desjardins, S. Noimark and W. Xia, *Sensors*, 2022, **22**, (17), 6417

Elastomeric nanocomposite coatings were used to enhance the photoacoustic visualisation of clinical needles. The coatings were applied to the exterior of the needle and the end-face of an optical fibre was positioned in the needle lumen. Visibility of the needle tip was achieved, and the performance was authenticated by an *ex vivo* tissue model. The needle was imaged out-of-plane and in-plane with an LED-based photoacoustic/ultrasound imaging system. Improvements in signal-to-noise ratios and visual enhancements were observed for both the needle tip and shaft. The enhanced visualisation achieved could be beneficial in ultrasound-guided minimally invasive surgeries.