JOHNSON MATTHEY TECHNOLOGY REVIEW

Johnson Matthey Highlights

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

EMISSION CONTROL TECHNOLOGIES

Increased NO2 Concentration in the Diesel Engine Exhaust for Improved Ag/Al2O3 Catalyst NH3-SCR Activity

The authors investigate the creation of higher NO2 concentration and its performance in the Ag/Al2O3 catalyst for the SCR route of eliminating NOx at low exhaust gas temperatures under real engine operation. The availability of NO2 concentration was increased for the SCR route with: (a) adding various NH3 and H2 mixtures upstream of the SCR catalyst and/or (b) using a Pt-based diesel oxidation catalyst (DOC) in front of the Ag/Al2O3-SCR catalyst. H2 improves the production of NO2 on the Ag/Al2O3 catalyst therefore the “Fast-SCR” like reaction is promoted by using the accessible NH3 primarily at low reaction temperature. The same effect was shown by the integration of the DOC in front of the Ag/Al2O3 as the NO2 availability was enhanced for the SCR process.

The Effect of Pt:Pd Ratio on Light-Duty Diesel Oxidation Catalyst Performance: An Experimental and Modelling Study
J. Etheridge, T. Watling, A. Izzard and M. Paterson, SAE Int. J. Engines, 2015, 8, (3), 1283

This article represents a section of a two-part investigation on the effect of Pt:Pd ratio at a constant total Pt+Pd loading of 120 g ft–3 on the catalytic activity of a DOC for light-duty operations. In this study a one-dimensional model able to estimate the effect of Pt:Pd ratio on DOC activity was developed. This model was based on an earlier model and certain parameters are changed to take into consideration the variation in Pt:Pd ratio. A function to aid the interpolation to any Pt:Pd ratio was used to describe the difference in each kinetic parameter with ratio. The NEDC test data with optimised kinetic parameters was used to develop the model and to obtain the best fit to measured data for each ratio. Good estimates of post-catalyst CO, THC and NO2 emissions over the NEDC across the entire range of Pt:Pd ratios were given by this model.

FINE CHEMICALS

Functional Thin Film Coatings Incorporating Gold Nanoparticles in a Transparent Conducting Fluorine Doped Tin Oxide Matrix

Gold nanoparticles (AuNPs) and F-doped SnO2 composites were combined by layering, making unique films which display interesting optoelectronic properties such as high visible transparency and electrical conductivity. Aerosol assisted chemical vapour deposition (AACVD) was used to deposit both layers onto heated glass substrates. The authors produced and analysed four sets of films: AuNPs, fluorine-doped SnO2 (FTO), a layer of AuNPs on FTO and an FTO layer on AuNPs. Changing the precursor concentration could alter the sizes of the AuNPs. Layered Au:FTO composite films were blue from the surface plasmon resonance of the AuNPs but demonstrate high transparency in the visible region and are electrically conducting. These are comparable to commercial FTO.

A Convenient Palladium-Catalyzed Azaindole Synthesis

Azaindoles are difficult to access but of interest for promising pipeline drug candidates. A reaction cascade...
involving enamine formation followed by intramolecular Heck reaction was investigated as a possible route. Palladium based catalyst systems and reaction systems were screened. The first generation XPhos catalyst was selective for a single regioisomer. Ultimately a one-pot synthesis was devised which provides direct access to azaindoles from amino-halopyridines and ketones.

NEW BUSINESS: FUEL CELLS

Effect of Particle Size and Operating Conditions on Pt$_3$Co PEMFC Cathode Catalyst Durability


The stability and performance of Pt catalysts has been proven to depend on particle size. To find out the effect of alloying and particle size in alloy catalysts, Pt$_3$Co catalysts with approximately the same Pt:Co:carbon ratio and three different mean particle sizes (4.9 nm, 8.1 nm, and 14.8 nm) were prepared by heat treatment. A higher degree of ordering was found in the larger particles. Systematic tests were carried out. The cathode based on 4.9 nm catalyst exhibited the highest initial electrochemical surface area (ECA) and mass activity, while the cathode based on 8.1 nm catalyst showed better initial performance at high currents. Accelerated performance loss testing using electrochemical decay protocols showed similar trends to previous Pt studies with higher initial performance for smaller particles but better durability for larger particles. Intermediate sized particles of ~8 nm provided the best balance of lifetime performance for Pt$_3$Co catalysts.

Performance Measurements and Modelling of the ORR on Fuel Cell Electrocatalysts – the Modified Double Trap Model


Results for the ORR in perchloric acid for ultra-low loading Pt/C electrodes have been experimentally obtained for various ORR mechanisms which were accomplished as a function of temperature (280–330 K), oxygen partial pressure (0.01–1) and potential (0.3–1.0 V vs. RHE). The results confirm the reaction exponent for oxygen of 1 ± 0.1 through the potential range of 0.3–0.85 V vs. RHE and show that as the overpotential rises the surface becomes progressively blocked towards ORR. This was not taken into account in the double trap model therefore the present authors have created an alternative version to include the formation of OOH$_{ad}$ intermediates. At higher overpotentials the OOH$_{ad}$ intermediates block the electrode and lead to a reduction in electrocatalyst performance compared to a Tafel type approximation. Hydrogen peroxide can also be formed by these intermediates at high overpotentials and is poorly described by models.

Optimal ADF STEM Imaging Parameters for Tilt-Robust Image Quantification


ADF STEM can be used to obtain useful qualitative data about the atomic scale structure of materials including catalysts. The present study used the cross section approach, a statistical method of counting atoms with the advantage that it is not affected by image parameter errors. An fcc Pt nanocube was analysed in order to demonstrate that small detector angles are helpful in avoiding problems caused by inaccurate tilt due to rotation of the nanoparticle samples under the beam. Optimised experimental parameters were devised and the balance between thermal diffuse scattering and elastic scattering is explained.

NEW BUSINESS: WATER TECHNOLOGIES

Structure and Properties of Highly Selective and Active Advanced Ion Exchange (AIX) Materials


There is a substantial loss of precious metal catalysts from active pharmaceutical ingredient (API) manufacturing processes into waste water streams. New composite materials for the recovery and purification of precious and base metals from API production, platinum group metals refining, base metal mining and metal processing industries have been developed. These materials are created either by grafting active adsorption sites on the outer surface and large pores of silica or joining polymeric chains of active adsorption sites to non-porous polymer fibres. The new AIX materials and conventional polystyrene resins are compared and the benefits are discussed.

Targeted Metal Purification by Scavenging


Transition metal catalysts used in any API manufacturing process must be reduced to an approved impurity limit in the final product. Highly potent APIs such as kinase inhibitors for cancer treatment pose a specific problem due to the low dosage required and the fact that they are synthesised using metal-catalysed aryl-aryl couplings or A-X couplings. Scavengers can remove metals and overcome problems such as the length of time required, meeting minimum contamination levels, avoiding product loss and solvent use. A large scale project to remove metal from APIs including kinase inhibitors was carried out using Johnson Matthey’s patented Sealed Flow Cartridge System. The main considerations were regulatory compliance (quality), cost and time. Implementation was tested from lab to plant scale and reduced the time taken to recover the
metal by a factor of 24, allowing the plant to reach its designed capacity.

**PRECIOUS METAL PRODUCTS: ADVANCED GLASS TECHNOLOGIES**

A Combined Single Crystal Neutron/X-Ray Diffraction and Solid-State Nuclear Magnetic Resonance Study of the Hybrid Perovskites CH$_3$NH$_3$PbX$_3$ (X = I, Br and Cl)


Hybrid perovskites such as methylammonium lead halide perovskites, CH$_3$NH$_3$PbX$_3$ (X = I, Br and Cl), are interesting as potential materials for photovoltaic devices. Variable temperature $^1$H and $^{13}$C magic angle spinning nuclear magnetic resonance (MAS-NMR) spectra were recorded for poly- and single crystalline samples of the perovskites. The CH$_3$NH$_3^+$ units were found to undergo dynamic reorientation due to tumbling of the organic component within the perovskite cage. Only the amine end of the CH$_3$NH$_3^+$ group was shown to interact with the inorganic network. Impedance spectroscopy showed that the conductivity changes significantly at the phase transition temperature, with implications for the performance of the photovoltaic device at higher temperatures. The optical band-gaps of each perovskite were determined using UV-visible spectroscopy confirming that they absorb strongly across the visible spectrum.

**PROCESS TECHNOLOGIES**

Reactivity of Oxygen Carriers for Chemical-Looping Combustion in Packed Bed Reactors under Pressurized Conditions


In order to effectively design, scale-up and optimise pressurised packed bed reactors for chemical-looping combustion (CLC) the influence of the pressure on the reactivity of the oxygen carriers must be understood. The authors have measured the redox reactivity of CuO/Al$_2$O$_3$ and NiO/CaAl$_2$O$_4$ particles at high pressures in a pressurised high-temperature magnetic suspension balance. Pressure has an adverse effect on the reactivity and this effect is kinetically controlled. This may be caused by the decline in the number of oxygen vacancies at elevated pressures. The reactant gas fraction is an important parameter and may possibly be associated to the contest between various species for adsorption on the oxygen carrier surface. A kinetic model was proposed taking these effects into consideration. A particle model which acknowledges diffusion limitations and kinetics was used to study these results on packed bed CLC applications with bigger oxygen carrier particles. It was concluded that at high pressure the diffusion limitation decreases due to reduced reaction rates and a rise in diffusion fluxes caused by Knudsen diffusion.

Continuous Catalytic Upgrading of Ethanol to n-Butanol and >C$_4$ Products Over Cu/CeO$_2$ Catalysts in Supercritical CO$_2$


n-Butanol (BuOH) has advantages over EtOH as a biofuel as it can transported and used in a gasoline engine with little or no modification, has a higher energy content, lower water miscibility and better gasoline compatibility. This paper uses a Cu-catalysed Guerbet reaction to investigate a more sustainable source of BuOH compared to the industrial OXO process, by upgrading EtOH. Six Cu catalysts on different supports were prepared and tested. Supercritical CO$_2$ was the solvent and was used in a continuous flow reactor. The high surface area CeO$_2$ support provided the best activity and gave over 30% yield and good selectivity. Increasing CO$_2$ pressure was found to improve the performance in this reaction possibly due to its effect on the support’s redox cycle.