CATALYSIS – APPLIED AND PHYSICAL ASPECTS

Pausing a Stir: Heterogeneous Catalysis in Dry Water

Dry water (DW) is a H₂O-in-air inverse foam, formed by mixing H₂O with hydrophobic silica particles (H18, Wacker Chemie) in a blender. This produces a free-flowing powder with ≤99% H₂O, comprising H₂O microdroplets where coalescence is prevented by a silica coating. Free-flowing DW-like powder 11 was prepared by blending an aqueous solution of maleic acid with H18 (5 wt% based on water) and 5 wt% Ru/Al₂O₃ catalyst. Hydrogenation to succinic acid was carried out by pressurising 11 with H₂ (20.7 bar) in a stainless steel autoclave. No stirring was used. The reaction was heated to 70ºC prior to introduction of H₂.

Separation of Different Metathesis Grubbs-Type Catalysts Using Organic Solvent Nanofiltration

A coupled reaction–separation process was used for the metathesis of 1-octene to 7-tetradecene and ethene. Grubbs-type Ru-based catalysts and the STARMEM™ series (active polyimide surfaces) of organic solvent nanofiltration (OSN) membranes were used. STARMEM™ 228 membrane separated the catalysts from their post-reaction mixtures to below 9 ppm of Ru. The coupled reaction–separation and recycling process increased the TON from 1400 for a single-pass reaction to 5500 for the overall consecutive reaction–separation steps of four cycles.

EMISSIONS CONTROL

Effect of Cobalt Oxide on Performance of Pd Catalysts for Lean-Burn Natural Gas Vehicles in the Presence and Absence of Water Vapor

Pd-based catalysts modified by Co were prepared by co-impregnation and sequential impregnation methods. The activity of the catalysts was tested in a simulated exhaust gas from lean-burn NGVs. The PdCo/La₂O₃ catalyst prepared by co-impregnation exhibited the best water-resistant performance. XPS analysis indicated that both CoAl₂O₄ and Co₃O₄ were present. For the catalyst prepared by sequential impregnation, the ratio of CoAl₂O₄/Co₃O₄ was higher than that of the catalyst prepared by co-impregnation.

FUEL CELLS

Recycling of Membrane Electrode Assembly of PEMFC by Acid Processing

PMFC catalyst coated membranes (CCMs) were dipped into H₂SO₄ until a transparent solution composed of Pt and Nafion perfluorosulfonic acid resin was formed. The membrane was dissolved, and the amorphous C catalyst support nanoparticles were oxidised. Subsequently, ~95% Pt and almost all the Nafion were recovered by centrifugal separation. The fuel cell performance of the recycled Nafion was close to that of virgin Nafion.

Experimental Validation of the “EasyTest Cell” Operational Principle for Autonomous MEA Characterization

The “EasyTest Cell” was validated by comparative electrochemical tests on MEAs in conventional PEMFC and PEM water electrolyser testing cells and the EasyTest Cell. The electrodes investigated were magnetron sputtered C/Ti/IrOₓ (IrOₓ 0.12–0.4 mg cm⁻²) and C/Ti/IrOₓ/Pt/IrOₓ (IrOₓ 0.08/Pt 0.06/IrOₓ 0.08 mg cm⁻²); C/Ti/Pt (0.15 and 0.25 mg cm⁻²) sputtered at various Ar pressures; and E-TEK ELAT® electrode (V21, Pt loading 0.5 mg cm⁻²). It is reported that the results demonstrate the reliability, simplicity and experimental possibilities of the EasyTest Cell.

Synthesis by Spray Pyrolysis of Mesoporous NbRu₃O₁₀ as Electro catalyst Supports in Fuel Cells

Spray pyrolysis was used to produce mesoporous powders of niobium oxide and niobium oxide with
12% Ru (by wt of metals). The NbO$_x$ and NbRu$_x$O$_y$ powders exhibited spherical particle morphology with internal mesoporosity introduced by surfactant templating, providing surface areas of 183 and 167 m$^2$ g$^{-1}$, respectively, after post-processing that included an acid etch and calcination. The electrical resistance of NbRu$_x$O$_y$ was reduced by ~5 orders of magnitude relative to NbO$_x$. CV showed that NbRu$_x$O$_y$ has activity for MeOH oxidation in basic solutions.

**METALLURGY AND MATERIALS**

**Melt Growth of ZnO Bulk Crystals in Ir Crucibles**


The thermochemical properties of ZnO make the growing of crystals difficult as it has a high melting point ($T_m = 1975$ºC) and undergoes thermal decomposition upon heating. The use of Ir crucibles is necessary. A thermodynamic analysis of melt growth of ZnO bulk crystals showed that the O$_2$ partial pressure in the surrounding vapour phase should be as low as possible during the heating cycle at lower temperatures in order to avoid Ir oxidation. Approaching the ZnO melting point, however, higher O$_2$ pressure is required to suppress ZnO decomposition. The required increase in O$_2$ supply with increasing temperature can be accomplished by the addition of CO$_2$ to the gas atmosphere. Experimental results confirmed these predictions.

**APPARATUS AND TECHNIQUE**

**Surface Characterization of Palladium-Alumina Sorbents for High-Temperature Capture of Mercury and Arsenic from Fuel Gas**


The interactions leading to the capture of Hg and As from fuel gas by Pd/Al$_2$O$_3$ sorbents were investigated. The adsorption of Hg is favoured by lower temperatures while As adsorption is favoured at 204–371ºC. The relative adsorption of Hg is suppressed in the presence of an excess of As. H$_2$S in the fuel gas moderates the adsorption of As while enhancing the adsorption of Hg. These differences in adsorption affinity of the Pd/Al$_2$O$_3$ sorbent can be overcome by adjusting the length and temperature of the adsorption bed.

**ELECTRICAL AND ELECTRONICS**

**Sputtered Amorphous Co–Pt–P Thin Films for Soft Underlayer of Perpendicular Magnetic Recording**


Amorphous Co-Pt-P thin films fabricated by DC sputtering were investigated by XRD and vibrating sample magnetometry. The maximum permeability of the Co-12 at% Pt-P films sputtered at RT was quite low when the P content was < 5.2 at%, but a Co-12 at% Pt-7 at% P thin film was amorphous and had a permeability of ~500. It had excellent soft magnetic properties with maximum permeability of 500, coercivity of 18 Oe and saturation magnetisation of 760 emu cm$^{-3}$. The film was gradually crystallised with increasing substrate temperatures; the crystallisation temperature was ~200ºC.

**Pd-Doped Sn–Ag–Cu–In Solder Material for High Drop/Shot Impact Reliability**


Pd was selected as a minor alloying element in a new Sn-1.2Ag-0.7Cu-0.4In solder alloy. Bar solder was studied for the tensile test, and solder balls were made for the rod drop impact test. The tensile properties and drop/shock reliability of Sn-1.2Ag-0.7Cu-0.4In-0.03Pd, were compared with those of Sn-1.0Ag-0.5Cu and Sn-3.0Ag-0.5Cu. The UTS, yield strength and elonga-
tion of 1 were superior to those of the other alloys tested. 1 exhibited outstanding drop/shock reliability.

MEDICAL AND DENTAL

Electrochemical Immunoassay for Human Chorionic Gonadotrophin Based on Pt Hollow Nanospheres and Silver/Titanium Dioxide Nanocomposite Matrix


An electrochemical immunoassay for human chorionic gonadotropin (hCG) assay has been developed. Ag nanoparticles were doped into TiO2 and chitosan colloids to form Ag–TiO2–chitosan nanocomposites. The free amino groups of chitosan were used to attach Pt hollow nanospheres for immobilisation of hCG. Optimal response of the immunoassay was achieved at pH 6.5 and 25ºC with an incubation time of 40 min. The immunoassay exhibited a linear range from 0.5 to 250 mIU ml–1 hCG with a detection limit of 0.26 mIU ml–1 at 3 × background noise.

A Photo-Caged Platinum(II) Complex That Increases Cytotoxicity upon Light Activation


The Pt(II) photocaged complex, [Pt(cage)], 1, contains a photolabile nitrophenyl group incorporated into the backbone of a tetradentate ligand that contains two pyridyl and two amide nitrogen donor sites. Activation of 1 with UV light cleaves the ligand backbone, releasing a Pt(II) complex, 2, that more readily exchanges its ligands. 1 is non-toxic to human breast cancer MCF-7 cells in the dark, whereas brief UV exposure induces cell death of MCF-7 cells at a level approaching that of cisplatin.

PHOTOCONVERSION

Platinum-Nanoparticle-Loaded Bismuth Oxide: an Efficient Plasmonic Photocatalyst Active under Visible Light

R. Li, W. Chen, H. Kobayashi and C. Ma, Green Chem., 2010, 12, (2), 212–215

Bi2O3 loaded with Pt nanoparticles was prepared via a simple photoreduction method. Pt/Bi2O3 was shown to act as a photocatalyst for the decomposition of the pollutants acetaldehyde, formaldehyde and methanol under visible light. The positive conduction band level of Bi2O3, which is able to transfer plasmon-induced electrons from the Pt nanoparticles, plays an important role in the catalytic properties of Pt/Bi2O3.

Artificial Inorganic Leaves for Efficient Photochemical Hydrogen Production Inspired by Natural Photosynthesis


Artificial inorganic leaves were developed by organis- ing light harvesting, photoinduced charge separation and catalysis modules (Pt/N-TiO2) into leaf-shaped hierarchical structures using natural leaves as biotemplates. The TiO2 catalyst is doped with nitrogen originating from the plant. Pt nanoparticles were grown on the surface of the artificial inorganic leaf (AIL)-TiO2 by irradiating AIL-TiO2 in 20% aqueous MeOH containing 2 wt% H2PtCl6·6H2O. The enhanced light-harvesting and photocatalytic watersplitting activities exhibited are due to the reproduction of the leaves’ complex structures and self-doping with N.

SURFACE COATINGS

Electrochemical Preparation and Characterization of Thin Deposits of Pd-Noble Metal Alloys


The electrochemical deposition of Pd-Au, Pd-Pt, Pd-Rh and Pd-Pt-Rh from chloride solutions is described. These deposits were characterised electrochemically in H2SO4 solutions by CV. The surface morphology of the alloys was examined by SEM and STM. The alloy surface composition was investigated in situ by an electrochemical method and ex situ by AES, while the bulk composition was determined by EDX analysis and AAS.