

Patents

CATALYSIS – APPLIED AND PHYSICAL ASPECTS

Platinum Nanoparticles Supported on Bacterial Cells

Japan Atomic Energy Agency, *Japanese Appl.* 2010-162,442

A cost-effective method for producing 0.1–50 nm nanoparticles of pgms, specifically Pt, is claimed. Aerobically-cultured iron-reducing bacteria such as *Shewanella putrefaciens* are contacted under aerobic conditions with a solution of Pt ions and either an organic acid or H_{2(g)} as electron donor. Pt nanoparticles are precipitated on the surface of the bacterial cells, which can in turn be deposited on a support such as diatomaceous earth, and are suitable for use as hydrogen isotope exchange reaction catalysts.

CATALYSIS – INDUSTRIAL PROCESS

'Self-Activating' Catalysts for Mercury Oxidation

US Department of Energy, *US Patent* 7,776,780 (2010)

Two classes of catalysts for Hg removal from industrial off-gas are described: metallic Ir or 5–10 wt% Ir-Pt alloy, which are corrosion resistant; and partially combusted coal with 20–80 wt% ash, which is disposable. Both are easily regenerated and are found to be activated *in situ* by exposure to HCl and Cl₂. The catalysts promote the oxidation of Hg to HgCl₂, allowing it to be removed by conventional scrubbers or precipitators.

CATALYSIS – REACTIONS

Novel Ruthenium-Based Olefin Metathesis Catalysts

Idenix Pharmaceuticals, Inc, *World Appl.* 2010/090,976

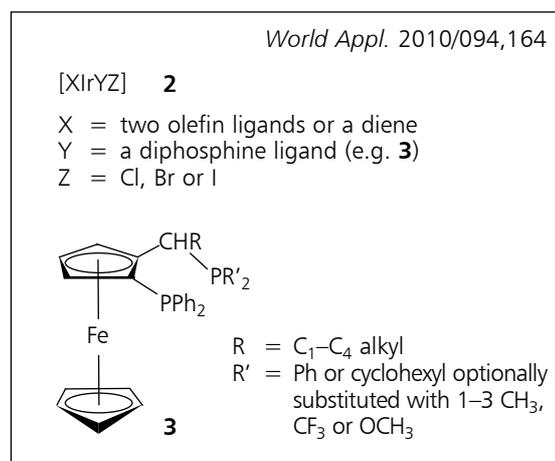
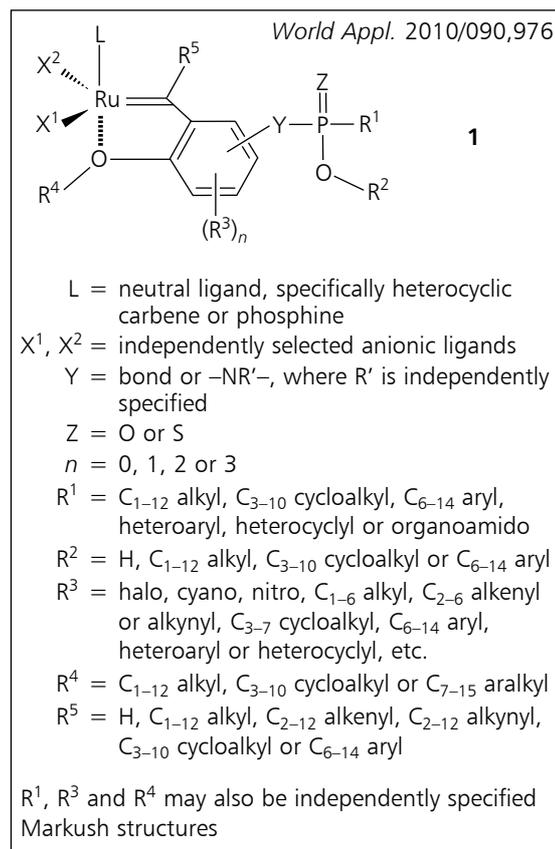
Phosphinate Ru complexes of general formula **1** and their use as catalysts for olefin metathesis and RCM are claimed. Typical molar ratios of catalyst to olefin are ≤0.5, preferably ≤0.01. The complexes may deliver benefits such as better yield, improved chiral purity and less metal contamination of the product.

Iridium Complexes for Imine Hydrogenation

Cheminova A/S, *World Appl.* 2010/094,164

A process for the hydrogenation of imines at 10–70°C and 10–100 bar in the presence of 0.001–5 mol% of an Ir-based catalyst with one ditertiary phosphine ligand and 0.01–1 mol% of a co-catalyst with a C–halogen bond is claimed. Specifically, the process can be used

for the asymmetric hydrogenation of a prochiral ketimine, in the presence of a chiral Ir catalyst of formula for example **2**, with one diphosphine ligand of formula for example **3**, to produce an optical isomer of an amine with ee >80%.



Osmium-Catalysed Hydrogenolysis of Sugar Alcohols

Chemtex Italia Srl, *World Appl.* 2010/119,351

Hydrogenolysis of polyalcohols such as sorbitol to lower diols, specifically propylene glycol, is conducted by contacting the alcohol with a suspension of a heterogeneous Os catalyst in water in the presence of a base such as Ba(OH)₂ and in the absence of any phosphine, at 30–90 bar and 180–250°C for 1–6 h. The Os catalyst is prepared by reducing OsCl₃ or OsO₄ with H₂ at 50–300°C to metallic Os dispersed at 1–6 wt% on a high surface area (>700 m² g⁻¹) support such as activated C or zeolite NH4Y.

Ruthenium-Catalysed Water Photolysis

Honda Motor Co, Ltd, *Japanese Appl.* 2010-158,627

A process for the production of H₂ from water uses Ru-based photocatalysts selected from soluble compounds of Ru with OAc⁻ and Cl⁻ or BF₄⁻, or insoluble compounds of Ru with terephthalate and Cl⁻, BF₄⁻, PF₆⁻ or Br⁻. These are added to water containing a solution of a photosensitiser such as Ru(bpy)₃Cl₂, a sacrificial electron donor such as disodium EDTA, and an electron-conducting substance such as methylviologen, and the mixture is irradiated with visible light of wavelength >420 nm. Depending on the compound, TONs of 3.9–93.4 were demonstrated experimentally.

EMISSIONS CONTROL

Exhaust System with Optimised Rhodium Activity

Mazda Motor Corp, *US Patent* 7,785,545 (2010)

A catalyst system comprising a close-coupled catalyst, **1**, and an underfloor catalyst, **2**, is formulated to prevent oxidation and deactivation of Rh under fluctuating air:fuel ratios by restricting Rh-doped Ce-Zr-Nd mixed oxide to catalyst **2**. The dissolved Rh is then reduced to active metal by HC and CO passing through catalyst **1** unreacted. Catalyst **2** further contains Pt/Al₂O₃ to convert HC to CO for more effective reduction. Catalyst **1** has a lower layer containing undoped Ce-Zr-Nd mixed oxide and supported Pd, and an upper layer with supported Rh.

NO_x Oxidation and Storage Catalyst

GM Global Technol. Operations, Inc, *US Appl.* 2010/0,221,154

An oxidation catalyst for use in a catalytic system to control lean-burn engine emissions and its method of production are claimed. A washcoat of Pt and/or Pd is applied to the first zone of a substrate. A mixture of 50–100% Pt and Pd is applied to the rear or second

zone of the substrate with an additional NO_x storage material such as BaO and/or K₂O. Zone 1 oxidises CO and HC, while zone 2 oxidises NO and stores NO₂ until it can be released for downstream SCR (which occurs optimally at equimolar NO:NO₂).

FUEL CELLS

Platinum Alloy Catalyst for PAFC

Johnson Matthey Plc, *World Appl.* 2010/092,369

A ternary alloy particularly suitable for use as an ORR catalyst in PAFCs consists of (in at%): 46–75 Pt; 1–49 of Ni, Co, Cr, Cu, Ti or Mn; and 1–35 Ta or Nb, but excluding the alloys 66 Pt-20 Cr-14 Ta and 50 Pt-25 Co-Ta.

Platinum Phosphide Catalyst

Daimler AG, *World Appl.* 2010/105,187

A PtP₂ PEMFC catalyst with a cubic crystal structure and the method of its manufacture are claimed, with the catalyst described to exhibit enhanced activity and stability in an acidic environment. The PtP₂ is formed by combining Pt catalyst with a phosphiding agent such as elemental P, PH_{3(g)}, trioctylphosphine or a phosphide, and may form a surface layer on a Pt or Pt-transition metal core, where the transition metal is one or more of Co, Fe, Ni and Cu.

Ternary Alloy Fuel Cell Catalyst with High Activity

UTC Power Corp, *World Appl.* 2010/107,426

Pt, a first alloy metal and a second alloy metal are successively deposited on a carbon support by reduction of appropriate precursors and alloyed by subsequent calcination. Alloy composition is: 40–60 mol% Pt, 5–30 mol% of one or more of Ir, Rh and Pd, specifically Ir, and 20–50 mol% of one or more of Ti, Mn, Co, V, Cr, Ni, Cu, Zr and Fe. The alloy has an average particle size of <60 Å, and a lattice constant of ~3.78–3.83 Å.

APPARATUS AND TECHNIQUE

Application of Palladium Salt to Cut Tobacco

Philip Morris USA Inc, *US Patent* 7,819,123 (2010)

A low-pH method of Pd salt addition to tobacco for the removal of polycyclic aromatic hydrocarbons from smoked product minimises the number of processing steps required. A solution of Na₂PdCl₄, K₂PdCl₄ or (NH₄)₂PdCl₄ is sprayed onto tobacco cut filler at 12–45% oven volatiles and at a mass loading of 0.01–0.15% relative to tobacco weight. The ratio of Pd:Cl is controlled to maintain >99% Pd solubility.

ELECTRICAL AND ELECTRONICS

Palladium Diffusion to Alter Semiconductivity Type

ABB Technology AG, *European Appl.* 2,234,144 (2010)

A wafer with two or more layers of different conductivity types is formed by: (a) depositing a 1 nm to 10 μm -thick layer of Pd on the first main side of an n-doped wafer; (b) irradiating this side to create defects at a depth controlled by the energy of radiation; and (c) diffusing the Pd into the wafer at 600–650°C to create a p-doped layer by replacing the defects. The process can be repeated at different depths and on the opposite side, and lateral variation can be achieved by using a thicker layer of Pd ($\leq 150 \mu\text{m}$) as a radiation mask. Electrical contacts are then created on opposite main sides of the wafer to form a power semiconductor device.

ELECTROCHEMISTRY

Aluminium Battery with Platinum Cathode

Equos Research Co, Ltd, *Japanese Appl.* 2010-129,495

A battery based on the principle of an air battery has an Al plate anode and a Pt plate cathode, both immersed in a non-aqueous ionic liquid as the electrolyte, and separated by a gel membrane which is impermeable to ions other than OH^- . The electrolyte is a mixed molten salt of 1-ethyl-3-methylimidazolium chloride and anhydrous AlCl_3 , in a molar ratio of 1:2 on the anode side of the membrane, and 2:1 on the cathode side. O_2 is bubbled over the Pt plate from a gas introduction pipe to facilitate the electrochemical reaction, which is found to proceed safely and efficiently.

MEDICAL AND DENTAL

Palladium-Titanium Braze for Ceramic-Titanium Bond

Boston Scientific Neuromodulation Corp, *US Patent* 7,771,838 (2010)

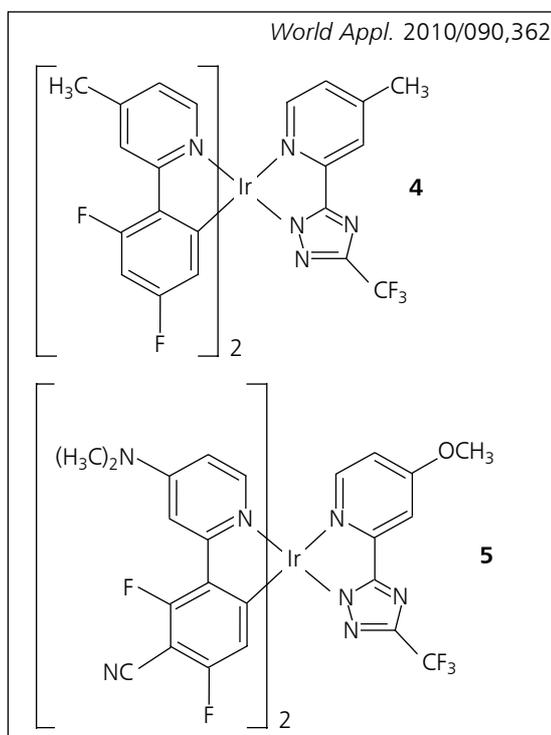
A method and material for forming an hermetic seal between ceramic and titanium sections of the housing of an implantable medical device is claimed. An interlayer comprising a Pd foil and a Ti foil, or a Ti foil sandwiched between two Pd foils, is placed at the interface of the two sections and pressure is applied during heat treatment under vacuum or inert gas. After melting and subsequent cooling, the interlayer forms an eutectic bond with the Ti and wets the ceramic for a complete seal.

PHOTOCONVERSION

Blue-Shifted Phosphorescent Iridium Complex

Pusan National University: Industry-University Cooperation Foundation, *World Appl.* 2010/090,362

Ir complexes containing a pyridyl triazole ligand with at least one substituent on the pyridine ring, for example **4** and **5**, exhibit improved phosphorescent quantum yields, particularly at short wavelengths. Wavelengths of peak intensity are typically $\sim 456 \text{ nm}$ and $\sim 486 \text{ nm}$. The Ir complexes are used in the emissive layer of OLEDs, with or without a host material. Synthesis methods are described.



SURFACE COATINGS

Platinum 'Paint' for Thermal Barrier Coating

Snecma Moteurs, *US Appl.* 2010/0,247,755

A pre-layer is formed on the binding sub-layer of a thermal barrier coating on a turbine blade and allows for efficient localised repair of the coating without stripping or modification. A suspension of pgm powder, specifically Pt, in water, oil or hydrocarbon liquid is applied to an aluminide sub-layer using a brush or spray gun or by dip-coating, and is diffusion heat-treated to form a layer of thickness 1–30 μm , preferably 2–10 μm .