

Patents

CATALYSIS – APPLIED AND PHYSICAL ASPECTS

Surfactant- and Polymer-Free Colloidal Platinum

Tanaka Kikinzoku Kogyo KK, *Japanese Appl.* 2009-228,067

A stable colloidal solution with 300–20,000 ppm Pt which can be used in catalyst preparation is produced without the need for a protective agent. A Pt salt such as $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ is dissolved in water or water and an organic solvent, and NaOH and/or NaHCO_3 is added to adjust the pH to 7.0–8.5. An inert gas is bubbled through the solution to lower dissolved O_2 to <1.0 ppm. The Pt salt is then reduced to Pt metal particles, preferably using EtOH, at 80–92°C. Ultrafiltration of the reduced solution adjusts electrical conductivity to <100 mS m^{-1} and pH to 7.0–12.0, and the pH may be further adjusted using NaOH.

CATALYSIS – INDUSTRIAL PROCESS

Rhodium-Catalysed Synthesis of Lactic Acid Esters

Uhde GmbH, *European Appl.* 2,141,145; 2010

A process for the synthesis of enantiopure lactic acid esters is claimed. Asymmetric hydrogenation of prochiral α -acetoxy acrylic acid esters in the presence of 0.1–2 mol% Rh-based catalyst and in a solvent such as propylene carbonate is carried out in an autoclave at 20–40°C under H_2 pressure of 1–20 bar. The catalyst or precatalyst is a Rh–bisphospholane complex such as $[\text{Rh}(\text{L})(1,5\text{-cyclooctadiene})]\text{BF}_4$ or $[\text{Rh}(\text{L})(\text{norbornadiene})]\text{BF}_4$ where the ligands L are heterocyclic phosphines which may be selected from: BASPHOS, binaphane, one of the DuPhos family or one of the catASium[®] M series.

Production of Fuel Gas from Waste Paper

Natl. Inst. Adv. Ind. Sci. Technol., *Japanese Appl.* 2009-197,223

A method for the production of biogas from waste paper such as shredded paper that is unsuitable for recycling is claimed. Water and paper in a mass ratio of between 1–100 are heated to 200–450°C in the presence of a catalyst such as 5 wt% Ru on activated carbon. A typical batch reaction at the laboratory scale gives cellulose conversion efficiency of 100% and yields fuel gas consisting of 48% CO_2 , 47% CH_4 , 5% H_2 and containing no organic carbon.

CATALYSIS – REACTIONS

Preparation of High Purity Duloxetine

Krka, dd, Novo mesto, *World Appl.* 2010/003,942

Enantiomerically-enriched alcohol precursors for duloxetine are prepared *via* asymmetric transfer hydrogenation (ATH) of β -keto amines with an optionally protected amino group. The catalyst is a chiral Ru or Rh (preferably Ru) complex prepared from a metal source such as $[\text{RuCl}_2(p\text{-cymene})]_2$ and a chiral ligand such as (*S,S*)- Me_2NSO_2 -1,2-diphenylethylenediamine, which is preferably of >99% enantiomeric purity. The ATH can be carried out in a solvent at 0–70°C, in the presence of one or more H donors such as 2-propanol or formic acid. Resulting product enantiomeric and chemical purities are >98%.

EMISSIONS CONTROL

Layered Three-Way Catalyst

Toyota Jidosha KK, *World Appl.* 2010/001,226

A TWC has two catalyst layers deposited on a channeled substrate. The lower layer has 0.25–5.0 g l^{-1} of each of Pt and/or Pd, with Pd deposited upstream of Pt and forming 20–45% of the length if present. As the exhaust gas first contacts Pd, Pt is exposed to cooler and less oxidising conditions and thermal deterioration is minimised. The upper layer has 0.1–1.2 g l^{-1} Rh and is 10–50% shorter than the lower layer so that both layers are exposed to the exhaust gas for optimal conversion, while Rh and Pt are kept separate to prevent alloying.

Catalytic Fuel Additive

E. M. Cunningham, *US Appl.* 2009/0,298,674

An additive to promote more efficient hydrocarbon oxidation in an internal combustion engine consists of: (a) a Pt compound, specifically bis(2,4-pentanedionato)Pt; (b) a Pd compound, specifically bis(2,4-pentanedionato)Pd; (c) a Fe compound such as ferrocene; (d) a Mg compound such as Mg 2-ethylhexanoate; and (e) a Re- or Ce-containing carboxylate, in a liquid medium, specifically aromatic hydrocarbon 150. Pt and Pd are each present in amounts ~100–2000 ppm. It may either be independently delivered to the engine or added to the fuel.

FUEL CELLS

Electrode for DMFC

AMOMEDI Co, Ltd, *World Appl.* 2010/010,990

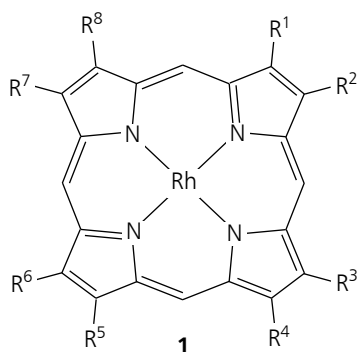
An electrode for a fuel cell is claimed, in which the Pt catalyst layer and the gas diffusion layer are integrated for improved efficiency. A nanofibre web, preferably 300–1000 μm thick with fibre diameter $<1 \mu\text{m}$, is formed by electrically spinning a solution of a carbon fibre precursor such as cellulose and is then oxidised and carbonised, and may include nanomaterials such as carbon nanotubes. The web is treated with a water-repellant fluorine-based resin, either on one or both sides, and has a final resistivity of $<11.5 \text{ m}\Omega \text{ cm}^2$. A Pt-based catalyst is deposited directly on the web, using a method such as vacuum deposition or spray coating.

Rhodium Porphyrin Catalyst

Natl. Inst. Adv. Ind. Sci. Technol., *Japanese Appl.* 2009-214,092

The Rh complex **1**, which may be supported on a conductive carrier such as carbon black, is claimed as a catalyst for electrochemical oxidation of CO. The complex can be used in the anode of a CO-fuelled PEMFC, or may be included in a device to remove CO from the

Japanese Appl. 2009-214,092



R^1-R^8 may be selected independently from:
H, alkyl, hydroxyalkyl, alkenyl, SO_3M^1
or $\text{R}^9\text{CO}_2\text{M}^2$

where:

$\text{M}^1 = \text{H}, \text{NH}_4$ or alkali metal

$\text{R}^9 = \text{iso- or normal alkenyl}$

$\text{M}^2 = \text{H}, \text{alkali metal or alkyl}$

and at least one of $R^1-R^8 = \text{R}^9\text{CO}_2\text{M}^2$

anode gas of a fuel cell. It may also be used to regenerate a Pt catalyst which has been deactivated through CO poisoning, or in the sensor of a CO detector.

METALLURGY AND MATERIALS

Hot Corrosion Resistant Alloy

Iowa State Univ. Res. Found., Inc, *US Appl.* 2009/0,324,993

A pgm-containing alloy for use in bulk form or as a coating on gas turbine components is claimed. It consists of: ~3–20 at% of one or a mixture of Pt, Pd, Rh or Ru; <23 at% Al, where this amount can be limited as a function of the concentrations of Ni and pgm so that no $\beta\text{-Ni-Al}$ phase is formed; at least one reactive element such as Hf, Y, Zr, La, Ce, preferably including Hf and in an amount 0.5–1 at% (or up to 2 at% if Si is present); and the balance Ni. It may also include 3–20 at% Cr, preferably 5–15 at%, and/or 7 at% Si. Al and Ni are present in the γ' phase.

High-Lustre Platinum Alloy

Citizen Holdings Co Ltd, *Japanese Appl.* 2009-221,536

A jewellery alloy is described as having high hardness for scratch resistance while maintaining the characteristic appearance of pure Pt. The Pt alloy is formed by first adding $\leq 2.0\%$ B to $\geq 98.0\%$ Pd (by weight) to obtain a uniform Pd-B alloy, then: (a) dissolving $\leq 5.0\%$ of this Pd-B alloy in $\geq 95.0\%$ Pt; or (b) dissolving $\leq 0.5\%$ of the Pd-B alloy and $<1.0\%$ of one or more of Nb, Ta, Ti and Zr in $\geq 99.0\%$ Pt.

APPARATUS AND TECHNIQUE

Flange for Direct Resistance Heating of Platinum Vessels

Corning Inc, *World Appl.* 2009/108,314

A disc-shaped flange for heating a vessel carrying molten glass consists of concentric rings. The inner rings are composed of a similar high-temperature Pt alloy ($>80\%$ Pt, e.g. 10RhPt) to that of the exterior wall of the vessel, to which the innermost ring of the flange is welded. The outer rings are composed of $>99\%$ Ni alloy and receive electric current from a bus bar. Heating occurs as current flows through the Pt-containing rings, which are constructed to minimise heat loss through the flange and ensure optimal heating of the vessel wall. An intermediate ring of Pt-Ni alloy with $>77\%$ Pt may also be included.

Palladium Membrane and Support

Los Alamos Natl. Secur. LLC, *US Patent* 7,611,565; 2009

A device for H₂ separation incorporates a thin, uniform Pd or Pd alloy membrane deposited on a porous support consisting of spherical microparticles, formed preferably of (in wt%) Fe₈₂Al₁₆Cr₂ and coated with an atomic diffusion layer of Al₂O₃ that is substantially incapable of H₂ reduction. The pores of the support are sized 0.05–0.5 μm, preferably 0.1–0.3 μm, and sintering at 975°C for 4 h may be used to achieve a narrower pore size range.

BIOMEDICAL AND DENTAL

Novel Route to Platinum Anticancer Compounds

Johnson Matthey Plc, *World Appl.* 2009/150,448

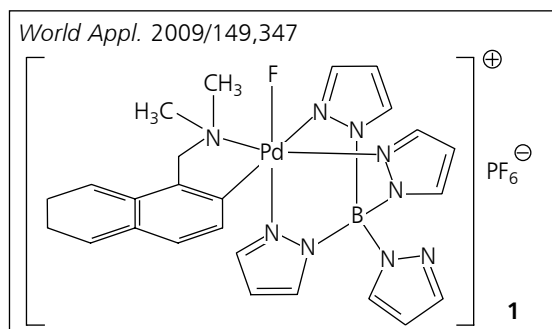
X[PtCl₃(NH₃)] where X is an alkali metal ion, preferably K⁺, is produced *via* the intermediate (NBu₄)[PtCl₃(NH₃)] and can be used in the synthesis of Pt anticancer compounds, specifically *cis*-[PtCl₂(NH₃)(2-picoline)]. A mixture of cisplatin, concentrated HCl, NBu₄OH_(aq), saturated NaCl_(aq) and a Pt catalyst, specifically Pt black, in an organic solvent such as chlorobenzene is heated, preferably at reflux, to form (NBu₄)[PtCl₃(NH₃)], which is separated from the mixture and concentrated before being reacted with an alkali metal salt in an alcohol. For example, reaction with KOAc in EtOH yields 50–60% K[PtCl₃(NH₃)·H₂O].

CHEMISTRY

Palladium(IV) Fluoride Complexes

Pres. Fell. Harvard College, *World Appl.* 2009/149,347

High-valent Pd–F complexes, typically Pd(IV)–F complexes such as **1**, which are stabilised by the inclusion of two fixed multidentate ligands, and their method of preparation are claimed. They are applied in the fluo-



ration of organic compounds through the transfer of electrophilic F⁺, such as in the reaction with a Pd(II) aryl complex to yield a fluorinated aryl compound, and can specifically be applied in the preparation of ¹⁸F- or ¹⁹F-labelled imaging agents for positron emission tomography (PET).

ELECTRICAL AND ELECTRONICS

Deposition of Iridium Film on a Memory Capacitor

Tosoh Corp., *Japanese Appl.* 2009-235,439

A uniform thin film of Ir and/or Ir oxide is formed on a three-dimensional structure by spraying a solution of an Ir complex such as [Ir(ethylcyclopentadienyl)-(1,3-cyclohexadiene)] in a solvent such as EtOH onto a semiconductor substrate heated to just above the decomposition temperature of the Ir complex.

ELECTROCHEMISTRY

Iridium Oxide Electrode

Phelps Dodge Corp., *US Appl.* 2009/0,288,856

An anode for electrowinning consists of IrO₂ or a mixture of ~80 mol% IrO₂ and ~20 mol% Ta₂O₅ coated on a conductive substrate such as Ti. Two layers are present: the first has IrO₂ in the crystalline phase, formed by heating a solution of a suitable precursor to between 450–550°C; the second has amorphous IrO₂, formed by heating the precursor to between 340–430°C. The coating is described as potentially improving process efficiency of Cu electrowinning operations by reducing cell voltage by ~15%.

PHOTOCONVERSION

OLEDs for Hydroponics

University of Utah, *US Appl.* 2009/0,313,891

Polymers with a π-conjugated backbone containing Pt or Ir atoms and emitting phosphorescence and fluorescence at approximately equal levels are claimed. They are formed for example by incorporation of Pt atoms into bis-1,4[2-(4-ethylphenyl)ethynyl]benzene from selected amounts of a complex such as PtCl₂(PBU₃)₂. The polymers can be tuned to emit required levels of both blue-green and red visible light by varying the spacing of monomers carrying Pt or Ir atoms, and they are particularly suited to plant-growing applications.