

# Patents

## CATALYSIS – APPLIED AND PHYSICAL ASPECTS

### Producing a Ruthenium Catalyst

Kyoto University, *Japanese Appl.* 2013-115,378

A method for producing a Ru catalyst is claimed. Ru supported by a metal oxide is pretreated with an aldehyde compound, a phosphorus compound and a lower alcohol compound. This Ru catalyst can be used for producing an alkyl group- or alkenyl group-substituted compound. Treating this tris(acetylacetonato) Ru catalyst supported on cerium oxide with formaldehyde, triphenylphosphine and methoxyethanol gave a catalyst useful for adding styrene on  $\alpha$ -tetralone.

### Manufacture of Supported Ruthenium Oxide

Sumitomo Chemical Co, Ltd, *Japanese Appl.* 2013-169,517

A supported Ru oxide is manufactured by contact treatment of a support with a solution containing a Ru compound, drying in a gas stream while stirring, and firing in an oxidising gas atmosphere. Preferably, the support contains  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$  and/or  $\text{SiO}_2$ . The supported Ru oxide is used in preparation of  $\text{Cl}_2$  by oxidation of HCl.

### Magnetic Nanoparticle Supported Osmium Oxide Catalyst

National Institute of Advanced Industrial Science & Technology, *Japanese Appl.* 2013-181,025

Magnetic nanoparticle ( $\text{Fe}_3\text{O}_4$ ) supported Os oxide catalysts for dihydroxylation of an olefin are prepared. During dihydroxylation the title catalysts exhibit little leaching of Os. As an example, a  $\text{Fe}_3\text{O}_4$  nanoparticle supported compound was synthesised by reaction of  $\text{Fe}_3\text{O}_4$ ,  $\text{K}_2\text{OsO}_4$  and a precursor. The compound is used as a catalyst for dihydroxylation of trans- $\beta$ -methylstyrene.

## CATALYSIS – INDUSTRIAL PROCESS

### Electrically Insulating Material using Platinum Catalyst

OAQ KZSK, *Russian Patent*, 2,490,739; 2013

Insulating material is claimed based on addition curing a silicone rubber containing both vinyl and hydride-containing silicones and fillers, crosslinked

under the influence of a Pt catalyst. The silicone rubber contains 40–70 wt% of a cyano-organophosphorus compound and/or 10–150 wt% of a modified aluminium hydroxide with respect to the amount of polyorganosiloxane.

## CATALYSIS – REACTIONS

### Producing Ethanol Using Rhodium Catalysts

Celanese International Corporation, *US Appl.* 2013/8,536,383

A process for producing ethanol involves hydrogenating acetic acid in the presence of a hydrogenation catalyst containing Rh and Sn. The molar ratio of Rh to Sn is from 20:80 to 80:20. The Rh and Sn are present in 0.1 wt% to 25 wt% based on total weight of the catalyst; the metal loading of rhodium is from 0.5 wt% to 2 wt%. The catalyst may further contain an active metal selected from Co, Zn, Cr, Cu, Pt, Pd, Ni, Fe, W, Mo, V and combinations thereof. The hydrogenation is performed in the vapour phase at a temperature from 250–375°C; with a pressure of 10 kPa to 3000 kPa, and a hydrogen to acetic acid mole ratio greater than 4:1. The support is selected from silica, silica/alumina, pyrogenic silica, high purity silica, carbon, alumina, and mixtures thereof. This support is present in 25 wt% to 99 wt%, based on total weight of the catalyst. The acetic acid conversion is greater than 30%.

## EMISSIONS CONTROL

### Palladium and Gold Catalysts

WGCH Technology Ltd, *US Appl.* 2013/0,217,566

An emission control catalyst for treating an engine exhaust includes an oxide carrier, and Pd particles and Au particles supported on the oxide carrier. The catalyst has a Pd to Au weight ratio in a range of about 0.5:1 to about 1:0.5. The emission control catalyst further comprises a substrate having a honeycomb structure with gas flow channels, wherein the oxide carrier and the Pd and Au particles are coated on the walls of the gas flow channels. A second oxide carrier may have Pt and Pd particles. An example is given of a supported catalyst containing 1% Pd and 2% Au prepared by adding 1% Pd, 2% Au colloid solution to a flask while stirring; adding MI-386 alumina powder to the flask, and then stirring the mixture for 18 h. The

mixture is then filtered and dried at 130°C for 3 h, and then ground to a fine powder. The powder is calcined in air at 500°C for 2 h using a heating ramp rate of 8°C min<sup>-1</sup>.

## FUEL CELLS

### Gas Diffusion Electrode Applying Platinum Nanowires

The University of Birmingham, *World Appl.* 2013/128,163

A gas diffusion electrode comprising a gas diffusion layer with a surface to which Pt nanowires have been applied and the surface is at least partially weakly hydrophobic or hydrophilic is claimed. The Pt nanowires are applied substantially or on regions of the surface. The surface area may be 50–100% weakly hydrophobic or hydrophilic. The gas diffusion layer has a water contact angle less than 130°. The Pt nanowires cover 75–99% of the total surface. These are uniformly distributed. The Pt nanowires are of length 50–500 nm, with a diameter 1–10 nm. The nanowires form a catalyst layer of thickness 50 nm–1 µm. The gas diffusion layer is selected from carbon cloth or carbon paper.

### Polymer Electrolyte Fuel Cells

Toshiba Corp, *Japanese Appl.* 2013-178,963

The title fuel cells have a MEA with a Ru-containing anode catalyst layer and a Pt-containing cathode catalyst layer. Either (i) a means for application of voltage above its open circuit voltage is provided or (ii) the anode catalyst layer, the electrolyte layer or their interface contains a catalyst to oxidise Ru(III) to Ru(IV) or Ru(III) adsorbent. The PEFC is operated with application of voltage higher than its open circuit voltage under open circuit conditions and the output can be recovered by reactivating the cathode catalyst.

## CHEMISTRY

### Manufacture of Aqueous Ruthenium Nitrate Solutions

Tanaka Noble Metal Industrial Co Ltd, *Japanese Appl.* 2013-180,936

Aqueous Ru nitrate solution of <1000 ppm Cl is prepared by neutralisation of a starting aqueous Ru nitrate solution with alkali hydroxide (e.g. KOH, to pH 8–13), rinsing the formed Ru hydroxide with dilute nitric acid ≥1 time(s) to remove the hydroxide-derived alkali

metals, then dissolving the rinsed Ru hydroxide in nitric acid.

## ELECTRICAL AND ELECTRONICS

### Structure Comprising Ruthenium Metal

Micron Technologies Inc, *US Appl.* 2013/0,221,420

A semiconductor device includes a smooth Ru metal layer which may form a capacitor bottom plate or a transistor gate such as a control gate. The smooth Ru may be on an oxide such as a gate oxide. The thickness of the Ru layer may be 150–800 Å and there may optionally be a capping material of thickness 100–500 Å.

### Ruthenium Seed Layer in a Magnetic Recording Medium

Hitachi Global Storage Technologies, *US Appl.* 2013/0,235,490

An apparatus is claimed with a perpendicular magnetic recording medium including a substrate, a soft underlayer above the substrate, a seed layer structure which contains Ru and a magnetic recording layer above the Ru seed layer. The seed layer structure is 10 nm or less in thickness. This structure has composition of NiW (2–10 at%) Ru (3–9 at%). The concentration of Ru is 3–9 at%.

## ELECTROCHEMISTRY

### Mesostructured Thin-Films as Electrocatalysts

V. Stamenkovic and N. Markovic, *US Appl.* 2013/0,209,898

The manufacturing of thin film catalysts comprises of (i) providing a substrate; (ii) providing a source of Pt group metal and alloying metal; (iii) using physical vapour deposition to deposit both metals; and (iv) annealing the thin film at a temperature of 300–400°C, forming a morphology of (111) hexagonal faceted surface grain structure in the thin film having a catalytic activity approaching Pt<sub>3</sub>Ni(111). The Pt group metal is selected from Pt, Pd and Rh. The transition metal is selected from Fe, Co, Ni, V and Ti. The thin film electrocatalyst thickness is about 5–20 nm.

## MEDICAL

### Platinum Based Antitumour Agent

Yamaguchi University, *Japanese Appl.* 2013-155,159

A polymeric antitumour agent characterised by containing an ionic complex of a Pt-based

antitumour agent and a styrene-maleic acid based copolymer is disclosed. The agent containing the ionic complex is accumulated in a tumour site due to enhanced permeability and retention effect. In an example, cisplatin and styrene-maleic acid copolymer were reacted, and the obtained ionic complex was freeze-dried to give stable nanoparticles, which inhibited proliferation of HeLa cells with an  $IC_{50}$  value of 104.1  $\mu\text{m}$ .

## NANOTECHNOLOGY

### Imaging Mass Analysis Using Platinum Nanoparticles

Nissan Chemical Industries Ltd, *World Appl.* 2013/122,225

A method for imaging mass analysis is characterised by preparing a sample by physical vapour deposition of Pt nanoparticles. This provides an improved method for imaging mass analysis using a matrix to assist in ionising a sample with high ionisation efficiency, reduction in visible information and migration, absence of interference peaks originating from the matrix and high spatial resolution.

## PHOTOCONVERSION

### Iridium Complexes Contained in Luminescent Materials

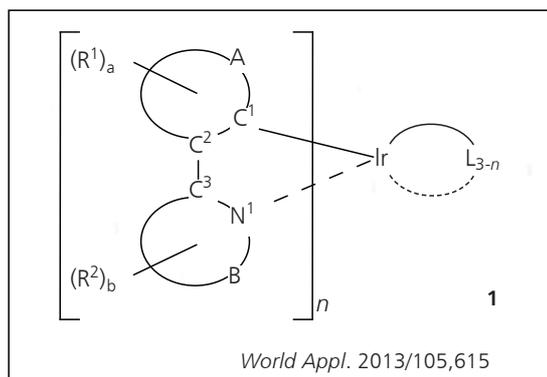
Mitsubishi Chemical Corp, *World Appl.* 2013/105,615

The title complexes show good organic solvent solubility and can be stored without precipitation. The title organic electroluminescent devices, preferably having emitter layers containing charge-transporting N-containing aromatic heterocyclic compounds as hosts and the complexes as dopants, have a low operating voltage and long service life. The title complexes are represented by **1** (A = 5- or 6-membered aromatic hydrocarbon ring or aromatic heterocycle including carbon atoms  $C^1$  and  $C^2$ ; B = 5- or 6-membered aromatic heterocycle including carbon atom  $C^3$  and nitrogen atom  $N^1$ ; L = organic ligand;  $p, q = 1-4$ ;  $n = 1-3$ ;  $R^1, R^2 =$  substituent;  $>1$  of  $R^1$  and  $R^2 = (Ar^1Z)_m X_m$ ; X =  $C_{6-20}$  (hetero)arylene;  $Ar^1 = C_{3-20}$  (hetero)aryl; Z =  $[C(R')_2]$ ;  $R' = H, F, Cl, Br, C_{1-20}$  alkyl, etc.;  $m = 1-3$ ;  $m1 = 0-3$ ;  $m2 = 1-20$ ).

### Platinum Phosphine Diphenyl Ether Derivative Complexes

Ube Industries, Ltd, *Japanese Appl.* 2013-155,131

The title complexes are represented by  $[L^1L^2Pt(o-C_6(R^{1-4}))_4X-o-C_6(R^{5-8}))_4]$  where X = O, S, NR<sup>9</sup>, silylene;  $R^9 = H, \text{halo}, (\text{cyclo})$



alkyl, alkenyl, aryl, aralkyl, alkoxy, arylalkoxy;  $R^1-R^8 = H, \text{halo}, (\text{cyclo})\text{alkyl}, \text{alkenyl}, \text{aryl}, \text{aralkyl}, \text{alkoxy}, \text{aryloxy}, \text{dialkylamino}, \text{alkylsilyl}$ ;  $L^1, L^2 =$  electronically neutral monodentate phosphine ligand;  $L^1L^2$  may form a bidentate phosphine ligand. The title complexes can be used in electroluminescent devices that emit light from blue to green.

## REFINING & RECOVERY

### Separating Platinum Sulfides

QAO Krastsvetmet, *Russian Patent*, 2,490,349; 2013

The invention involves pulping a concentrate of Pt and Re sulfides in an aqueous ammonia solution. The pulp is treated with hydrogen peroxide solution at a temperature of 25–45°C. This reaction mixture is acidified with sulfuric acid until a pH 0.2–2.0 is achieved. This is heated and aged. The precipitate of Pt compounds is separated from the solution by filtering. The effect is to enable separation of Pt at the step for extracting Re from a sulfide concentrate.

## SURFACE COATINGS

### Films with Absorbent Palladium Coating

Morgan Adhesives Company, *European Appl.* 2,626,379; 2013

A multilayer film has a polymeric film layer and an absorbent layer containing a Pd complex. The absorbent layer also contains at least one of a cyclodextrin, a hydrophobin protein, or a derivative thereof and is effective to absorb an odour, a volatile organic compound or both. The absorbent layer comprises between 0.1–0.75 wt% Pd complex, 2–7 wt% of cyclodextrin and 0.1–0.5 wt% of hydrophobin protein. The polymeric film layer comprises at least one of polyethylene, polypropylene, polyvinyl chloride and polyethylene terephthalate. The absorbent layer has a

surface area between 280–320 cm<sup>2</sup> and when placed in a chamber having a volume of 400 cm<sup>3</sup> with 2 ml of an *n*-butanol saturated atmosphere injected into the chamber it absorbs greater than 80% of the *n*-butanol in 1 h.

#### **Sulfonation of Plastic and Composite Materials**

M. Wojtaszek *et al.*, *US Appl.* 2013/0,209,689

A method of preparing a plastic article to accept plating is claimed. A portion of the plastic article is rendered plateable by sulfonation by: (i) exposing the plastic article to an atmosphere containing a sulfonating agent to sulfonate at least a portion of the plastic article; (ii) contacting the sulfonated plastic article with a conditioner; (iii) contacting the plastic article with a Pd metal activator so that the noble metal is adsorbed on at least a portion of the surface of the plastic article; and (iv) contacting the plastic article with an accelerator to react with the adsorbed Pd to increase the catalytic activity of the adsorbed noble metal towards plating. The plastic may be selected from poly(ether-ether-ketone) resins, polyamide, polyethylene, polypropylene, etc., or a combination. The sulfonating agent comprises fuming sulfuric acid or vapour phase sulfur trioxide. Timing of contact between the sulfonating agent and the plastic article is between 1 sec and 60 min.

#### **Obtaining Platinum Group Metal Coatings**

FGUP Radievyi Institut im. V. G. Khlopina, *Russian Appl.* 2,489,516; 2013

An invention to help obtain pore-free microcrystalline coatings with high adhesion to substrate materials is claimed. Coatings are obtained from Ir or Rh by a thermal decomposition process at a temperature between 250–450°C and pressure 0.01–0.05 mm Hg. The precursors are Ir tetratrifluorophosphine hydride of formula  $\text{HIr}(\text{PF}_3)_4$  or Rh tetratrifluorophosphine hydride of formula  $\text{HRh}(\text{PF}_3)_4$ .