

# Patents

## CATALYSIS – APPLIED AND PHYSICAL ASPECTS

### Ruthenium in Conversion of Synthesis Gas

Johnson Matthey Plc, *World Appl.* 2011/089,377

A method for the conversion of synthesis gas into HCs involves the following steps: (a) passing a mixture of H<sub>2</sub> and CO over a Co catalyst at 210–225°C under 5–60 bar abs to produce a reaction product mixture of HCs, steam, CO and H<sub>2</sub>; (b) condensing and separating the H<sub>2</sub>O to produce a dewatered product mixture; (c) passing the dewatered mixture over a supported Ru catalyst at 230–265°C under 30–60 bar abs; and (d) recovering the HCs. The support for the Ru catalyst is selected from oxidic support, graphite or silicon carbide. The Ru content of the catalyst is in 0.1–10 wt%, preferably 2.5–7.5 wt%. The Ru catalyst is a powder with a volume median diameter in the range 1–200 µm.

## CATALYSIS – REACTIONS

### Hydrogenation of 1,1-Difluoro-2-nitroethane

Bayer CropScience AG, *World Appl.* 2011/042,376

A process for producing 2,2-difluoroethylamine by hydrogenating 1,1-difluoro-2-nitroethane uses a catalyst selected from Pt, Pd, Rh, Ir, Os, Ru, Fe, Co and/or Ni, preferably Pt or Pd. The catalytic hydrogenation step involves introducing gaseous H<sub>2</sub> into the reaction vessel or generating H<sub>2</sub> *in situ*. The preferred catalysts are PtO<sub>2</sub>, Pd(OH)<sub>2</sub> on activated C or a Lindlar catalyst.

### Palladium in Production of Glyceric Acid

Rigas Tehniska Univ., *European Appl.* 2,332,899; 2011

A Pd catalyst is prepared for the selective production of glyceric acid. H<sub>2</sub>PdCl<sub>4</sub> in HCl is added to (C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>N solution in C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>, this is shaken and separated by a liquid extraction method. A carrier, selected from a group of inorganic nanopowders synthesised in plasma, is added to the Pd catalyst organic precursor obtained. This mixture is then dried, Pd is pyrolytically reduced by heating the mixture up to 573 K at 10–11 K min<sup>-1</sup> and calcination at 573–673 K for 4–5 min at 1 atm. The ratio of glycerol and Pd is n(glycerol)/n(Pd) = 300–500 mol/mol.

## EMISSIONS CONTROL

### Multiphase Three-Way Catalysts

Catalytic Solutions, Inc, *World Appl.* 2011/068,509

A TWC for the simultaneous conversion of NO<sub>x</sub>, CO and HC can consist of a perovskite and non-perovskite phase. The catalyst comprises a substrate, a washcoat and a multiphase catalyst represented by the general formula Ce<sub>y</sub>Ln<sub>1-x</sub>A<sub>x+s</sub>MO<sub>z</sub> (x < 1; y < 10; s < 10; z > 0, where s = 0 only when y > 0 and y = 0 only when s > 0), where A is selected from Mg, Ca, Sr, Ba, Li, Na, K, Cs and Rb; Ln is one or more lanthanides; and M is selected from Pt, Pd, Rh, Ru, Fe, Mn, Cr, Ni, Co, Cu, V, Zr, Ag, Au, Al, Ga, Mo, W or Ti. This composition has an additional precious metal component selected from Pt, Pd, Rh, Ir, Os, Ru and Ag.

### NOx Trap with Two Zones

Johnson Matthey Plc, *British Appl.* 2,476,573; 2011

A NO<sub>x</sub> trap consists of at least one pgm, preferably Pt and/or Pd, at least one NO<sub>x</sub> storage material and bulk CeO<sub>2</sub> or a bulk Ce-containing mixed oxide deposited uniformly in a first layer (which has a first upstream zone for oxidising HCs and CO) on a honeycombed substrate monolith. A second downstream zone consists of a dispersion of rare earth oxide and has increased heat generation during desulfation. The proportions of the first and second zones are from 20:80 to 80:20. The honeycombed substrate monolith of the first zone is coated, this is then dried and fired; the second zone is impregnated with an aqueous solution of a rare earth element, then this is also dried and fired.

### Destruction of Volatile Organic Compounds

Süd-Chemie Inc, *World Appl.* 2011/066,009

An oxidation catalyst for the destruction of CO, VOCs and halogenated VOCs is prepared by making an aqueous mixture slurry consisting of a solid solution of CeO<sub>2</sub> and ZrO<sub>2</sub> plus either Sn oxide and SiO<sub>2</sub> or both blended with a binder selected from colloidal Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub> and CeO<sub>2</sub>. The mixture is blended and coated to the substrate, which is produced from cordierite, mullite, Fe-Cr alloy and stainless steel and has a honeycomb or monolithic structure. The coated substrate is then dried and calcined, at least one of Pt and Ru are deposited on the calcined coated substrate and this is then dried and calcined. The ratio of Ru to

Pt is between 20:1 and 1:20 and the loading of Pt and Ru on the substrate is 0.35–7.1 g l<sup>-1</sup>.

## FUEL CELLS

### Platinum-Cobalt Nanocube Catalyst

Hyundai Motor Co, *US Appl.* 2011/0,118,111

A Pt-Co nanocube catalyst can be prepared by dissolving a Pt precursor, a Co precursor, a surface stabiliser and a reducing agent then heating at 120–200°C at the rate of 0.5–10°C min<sup>-1</sup> and the temperature of 200°C is maintained for 60–90 min in an inert gas atmosphere. The Pt-Co nanocube is then adsorbed on a C support (selected from ketjen black, CNT and fullerene) and the surface stabiliser is removed to obtain the catalyst. This method for preparing the catalyst allows the preparation of nanocubes with uniform size and cubic shape for high efficiency fuel cell applications.

### Iridium Catalyst in Fuel Cells

Nissan Motor Co, Ltd, *Japanese Appl.* 2011-040,177

Ir supported on C is used as a catalyst for the anode in a fuel cell. The catalyst layer is ≤6 μm thick and the loading of Ir is 0.01–0.3 mg cm<sup>-2</sup>. Corrosion of the anode C is prevented and fuel cell lifetime is prolonged.

## APPARATUS AND TECHNIQUE

### Protective Coating of Crucibles

Heraeus Quarzglas GmbH & Co KG, *US Patent* 7,955,715; 2011

A crucible for use at high temperature consists of a partial protective layer containing Ir, Os, Ru or Re, preferably Ir, and a base body of W. Ir content in the layer is 5–50 at%. The protective layer is prepared from a powder mixture containing W powder and the powder of the coating material and this is applied by flame spraying or plasma spraying the wall to be coated.

### Palladium Nanoparticles in Carbon Nanotubes

Univ. Central Florida Res. Found., Inc, *US Patent* 7,968,072; 2011

A novel method for preparing CNTs simultaneously formed and filled with Pd NPs using arc discharge (see **Figure**) in solution is claimed. A PdCl<sub>2</sub> solution is prepared using PdCl<sub>2</sub> powder, deionised water and HCl, a graphite electrode assembly is immersed in the solution and then, connected to a

DC power supply. The electrodes are then brought into contact to strike an arc, separated, and an arc-discharge is created at >3000°C. The PdCl<sub>2</sub> solution is vapourised to leave a residue of Pd NPs. Graphene layers are formed which roll away from the electrodes and simultaneously encapsulate the Pd NPs. These unique nanotube structures have potential as gas sensors or as means for hydrogen storage.

### Platinum-Based Electrode in Spark Plug

Federal-Mogul Ignition Co, *US Appl.* 2011/0,121,713

A spark plug consists of a metallic shell, an insulator, and centre and ground electrodes. The insulator is at least partially within the axial bore of the metallic shell, the centre electrode is at least partially within the axial bore of the insulator and the ground electrode is attached to a free end of the metallic shell. The material in the centre or ground electrodes or both is (in at%): ~50–99 Pt; ~5–20 Al; and ≤ 30 refractory metal selected from Ru, Ni, Re, Ta, W, Mo or a combination of these. At 500°C, a layer of Al<sub>2</sub>O<sub>3</sub> is formed on an outer surface of the centre electrode, the ground electrode or both.

## PHOTOCONVERSION

### Nitride-Based Light-Emitting Device

Samsung LED Co, Ltd, *European Appl.* 2,262,013; 2011

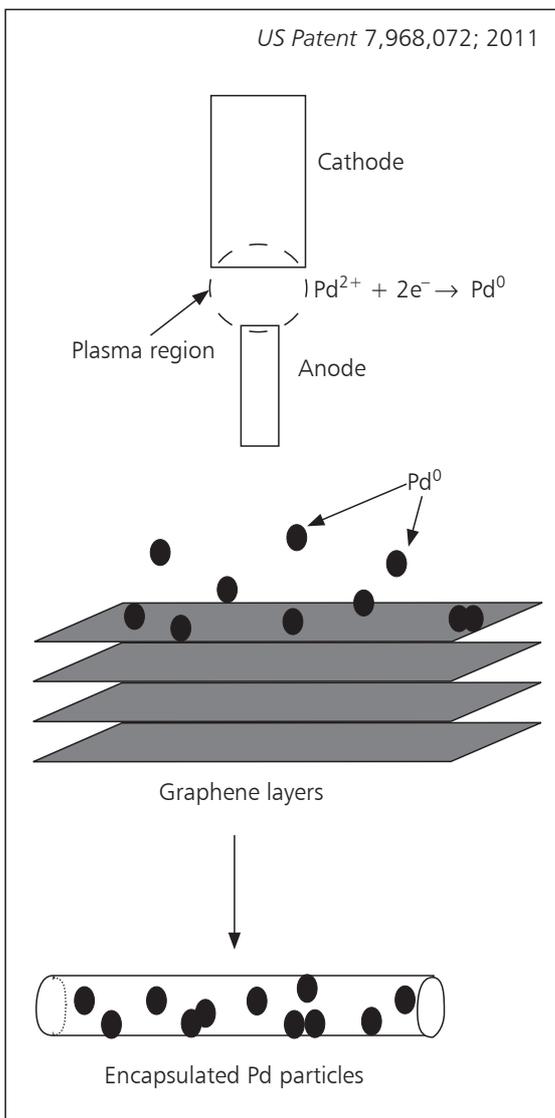
A nitride-based light-emitting device is composed of a substrate with an n-cladding layer, an active layer, a p-cladding layer, a Zn-containing oxide ohmic contact layer with a p-type dopant and a reflective layer consisting of at least one element selected from Pt, Rh, Ru, Ag, Al, Zn, Mg and Cr. The thickness of the ohmic contact layer is 0.1–1000 nm. A first and second electrode layer are selected from Pt, Pd, Ru, Ni, Au, Mg, Cu, Zn, Ag, Sc, Co, Li, Be, Ca, Re, Ti, Ta, Na and La. The first layer is inserted between the p-cladding layer and the ohmic contact layer and the second layer is inserted between the ohmic layer and the reflective layer.

## REFINING AND RECOVERY

### Recovering Precious Metals

Metals Recovery Technol. Inc, *US Patent* 7,935,173; 2011

A hydrometallurgical procedure for recovering Pt, Pd, Rh, Ir, Ru and Au involves separating the precious metals from the base metals in HCl and precipitating using substituted quaternary ammonium salt (SQAS)



of formula  $\text{H}_{0-3}\text{R}_{4-1}\text{NX}$ , where H = hydrogen, R = organic group, N = nitrogen and X = halide, preferably tetramethylammomium chloride. Pd is separated by precipitating as Pd-SQAS, the precipitate is added to water or acid, this is then boiled to solubilise the precipitated Pd-SQAS and any remaining precipitate is then removed. Pt and Ir are separated by precipitating as Pt-SQAS and Ir-SQAS, the remaining Pt-SQAS and Ir-SQAS precipitates are slurried in water,  $\text{NaNO}_2$  is added, Pt-SQAS precipitate is removed and Ir-SQAS is precipitated with HCl.

**Recovery of High Quality Rhodium Powder**

Sumitomo Metal Mining Co, Ltd, *Japanese Appl.* 2011-038,165

A process to obtain high quality Rh powder is described. This process involves the reduction roasting of the Rh-containing residue with Fe, followed by removal of Fe, carried out in the presence of  $\text{H}_2\text{SO}_4$ . The remaining solid is then dissolved in HCl and  $\text{H}_2\text{O}_2$  solution, then Rh is refined. This Rh black is subjected to a pretreatment heating stage at 200–400°C, then a first heating stage is performed in an inert gas atmosphere of 600–800°C. The sample undergoes a wet grinding and cleaning process then a second heating stage at 900–1100°C in an inert gas atmosphere.

**SURFACE COATINGS**

**Platinum-Catalysed Coating in Adhesive Tapes**

Bostik, Inc, *US Appl.* 2011/0,159,225

A conformable, pressure sensitive foam adhesive tape consists of a closed cell polyolefin foam core, a pressure sensitive adhesive on one side of this polyolefin foam core (this has a polyacrylate backbone and modified silyl functionality) and a release liner which has a Pt-catalysed polymeric polysiloxane coating. There is no control release agent in the release coating. The foam has a density of 300–800  $\text{kg m}^{-3}$  and a tensile strength in the range of 400–600 psi.