

Patents

CATALYSIS – APPLIED AND PHYSICAL ASPECTS

Clean Production of Solid Ruthenium Complex

Johnson Matthey PLC, *World Appl.* 2010/064,045

A cationic Ru complex is produced by reacting a $[\text{Ru}(\text{arene})(\text{halogen})_2]_2$ with a 4,4'-bis(disubstituted-phosphino)-3,3'-bipyridine ligand in at least one alcohol with boiling point $<120^\circ\text{C}$ at 1 atm. Preferred arenes are benzene, *p*-cymene or 1,3,5-trimethylbenzene; halogens are Cl, Br or I and ligands are PPhos, TolPPhos and XylPPhos. The complex may be used as a hydrogenation catalyst without solvent change. Further, a C_{1-10} alkane may be added to produce a solid complex, which exhibits improved stability over complexes precipitated with solvents such as MBTE.

Hydrothermally-Prepared Rhodium on Zeolite

Nippon Chem. Ind. Co, Ltd, *Japanese Appl.* 2010-029,787

A hydrothermal method for producing a catalyst with >1 wt% Rh highly dispersed on zeolite is claimed. An aqueous slurry of a high-silica zeolite; a water-soluble Rh salt, preferably Rh(III) nitrate; and a source of either tetraethylammonium or tetrapropylammonium as a templating agent, preferably tetraethylammonium hydroxide, is prepared. The molar ratio of water, Rh and templating agent is 1–50:0.001–0.03:0.01–1, based on Si in the zeolite. The mixture, with pH 10–14, is then treated at 140 – 180°C for ~ 40 – 70 h.

CATALYSIS – INDUSTRIAL PROCESS

PGM Catalyst for Upgrading Middle Distillates

Total Raffinage Marketing SA, *World Appl.* 2010/079,044

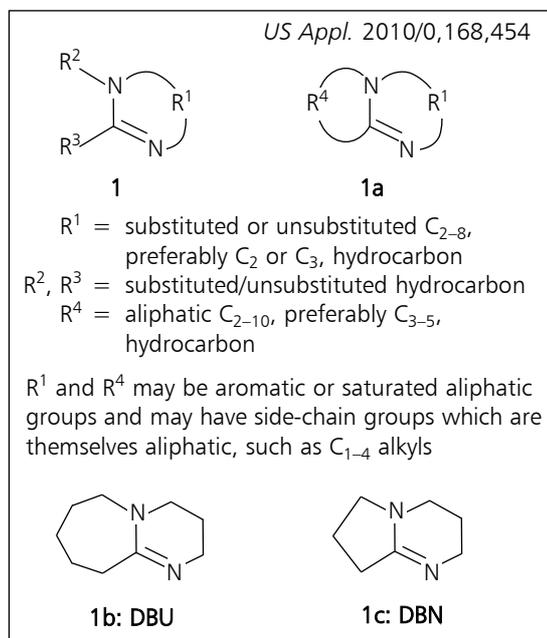
A feedstock such as light cycle oil with $\text{Cl} \leq 40$, $\text{CN} \leq 35$, $100 \text{ ppm} \leq \text{N} \leq 1200 \text{ ppm}$, $200 \text{ ppm} \leq \text{S} \leq 2.5 \text{ wt\%}$ and aromatics $\geq 50 \text{ wt\%}$, is in a first step passed over an HDS/HDN catalyst such as $\text{NiMo}/\text{Al}_2\text{O}_3$. The effluent, optionally stripped, is then hydrodearomatized over a catalyst containing 0.25–1 wt% of each of Pt and Pd highly dispersed on a SiO_2 – Al_2O_3 carrier with a pore volume of 0.6 ml g^{-1} and a surface area of $300 \text{ m}^2 \text{ g}^{-1}$. Reaction conditions are typically 0.5 – 1.2 h^{-1} LHSV, 250 – 320°C and 45–65 bar gauge pressure. The product obtained may have $\text{S} \leq 1 \text{ ppm}$, $\text{N} \leq 1 \text{ ppm}$, aromatics $\leq 2 \text{ wt\%}$, $35 \leq \text{Cl} \leq 43$ and $40 \leq \text{CN} \leq 48$, and is suitable for use in a diesel pool at $\geq 50 \text{ wt\%}$.

CATALYSIS – REACTIONS

Phosphorus-Free Rhodium Hydrogenation Catalyst

Schlumberger Technol. Corp, *US Appl.* 2010/0,168,454

Hydrogenation of $\text{C}=\text{C}$ or $\text{C}=\text{N}$ bonds in organic compounds is carried out in the presence of a Rh complex with non-phosphine ligands A and B, where A is a heterocyclic organic base, **1**, preferably **1a** and particularly 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), **1b**, or 1,5-diazabicyclo[5.3.0]non-5-ene (DBN), **1c**, and B is a cycloaliphatic diene, preferably 1,5-cyclooctadiene (COD).



EMISSIONS CONTROL

Three-Way Catalyst with Improved Sulfur Tolerance

Toyota Central Res. Dev. Labs, Inc, *Japanese Appl.* 2010-051,847

A dual-layer catalyst has: a first layer with 0.01–5 wt% Pt supported on CeO_2 – ZrO_2 ($\geq 45 \text{ wt\% CeO}_2$) and Al_2O_3 ($\leq 0.1 \text{ wt\% TiO}_2$); and a second layer with 0.01–5 wt% Rh supported on CeO_2 – ZrO_2 (4–35 wt% CeO_2) and TiO_2 – Al_2O_3 (5–20 wt% TiO_2). This formulation of the compound oxides is found to control S poisoning to limit formation of H_2S and further prevents degradation of OSC performance during high-temperature operation.

Catalyst for Removal of CO from Motorcycle Exhaust

Cataler Corp, *Japanese Appl.* 2010-058,069

A catalyst suitable for low-temperature use in motorcycles consists of a honeycomb substrate with two sections. The first stage has loadings (per litre substrate): 1–10 g Pd, preferably 2.5–6 g Pd; and 0.05–5 g Rh, preferably 0.15–1.5 g Rh. The second, downstream stage has loadings (per litre substrate): 0 g Pd and 0.05–5 g Rh, preferably 0.15–1.5 g Rh. The Pd in the first stage acts to raise the temperature of the exhaust gas, promoting oxidation of CO in the second stage, even under rich exhaust conditions.

FUEL CELLS

Quarternary Fuel Cell Catalyst

UTC Power Corp, *World Appl.* 2010/050,964

An alloy has composition $Pt_wV_xM_yIr_z$, where (in mol%): $30 \leq w \leq 75$, $5 \leq x \leq 50$, $5 \leq y \leq 50$ and $5 \leq z \leq 30$, and M is one or a combination of Co, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Mo and W. Specifically, the alloy is $Pt_{40}V_{20}Co_{30}Ir_{10}$ and is deposited at 10–70 wt% loading on a C support as particles 2–20 nm in size. As a cathode catalyst in a PEMFC, PAFC, SOFC or other fuel cell, the alloy is durable and has high ORR activity.

Platinum Mesh for Strengthening SOFC

Shinko Electr. Ind. Co, Ltd, *US Patent* 7,722,980 (2010)

A SOFC system has a cathode electrode layer and an anode electrode layer formed on opposite faces of a single solid oxide substrate, with both layers containing an embedded Pt mesh and the whole encased in an oxide layer formed from a solid electrolyte. The Pt mesh and oxide layer prevent cracking of the cell due to thermal shock, allowing the system to be heated by direct exposure to a flame with rapid start-up. The Pt meshes may also be connected to lead wires and function as current-collecting electrodes.

METALLURGY AND MATERIALS

Multilayer Coating for Costume Jewellery

Umico Galvanotechnik GmbH, *World Appl.* 2010/057,573

A base metal blank is successively plated with: (a) an optional first layer of 15–20 μm Cu; (b) a 1–3 μm layer of preferably pure Pd; (c) an optional intermediate layer of 0.1–0.2 μm Au; and (d) a 0.1–0.5 μm layer of either Pt-Ru with 60–75 wt% Pt, or Rh-Ru with 70–80 wt% Rh. Layers (b) and (d) are preferably

deposited by rack coating. The coating is found to have abrasion resistance which is much higher than the average resistance of the metals in (d). Good colour and brightness are also obtained.

Rhodium Alloy for Gas Turbine Repair

General Electric Co, *US Patent* 7,722,729 (2010)

An alloy with improved high-temperature performance is composed of (in at%): (a) $\geq 50\%$ Rh; (b) $\leq 49\%$ of one of Pt, Pd, Ir (or a combination); (c) 1–15%, preferably 1–6%, W and/or Re; (d) $\leq 10\%$, preferably $\leq 8\%$, Ru and/or Cr; and, optionally (e) $\leq 3\%$, preferably $\leq 2\%$, one or more of Zr, Y, Hf, Ta, Al, Ti, Sc, a lanthanide and an actinide. The sum of (a) and (b) is $\geq 75\%$, preferably $\geq 85\%$. The alloy contains ≥ 90 vol% of the A1-structured phase at $>1000^\circ\text{C}$. A method of using the alloy to repair components such as the blade tip, leading and trailing edges is also claimed.

Low-Melting Palladium Solder

K. Weinstein, *US Patent* 7,722,806 (2010)

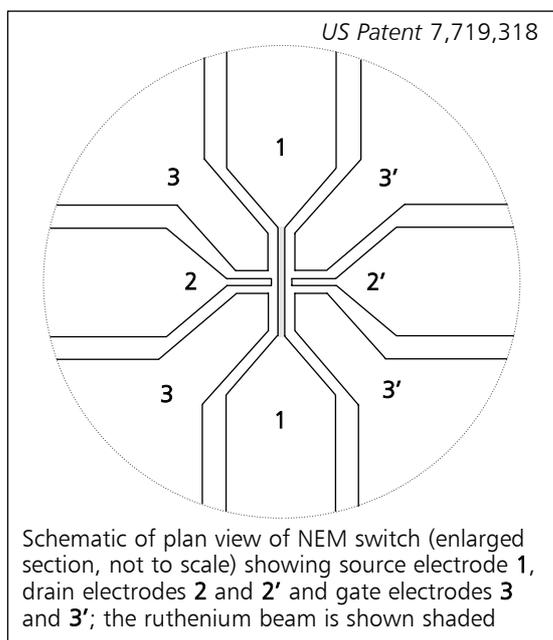
A solder for use with Ni-free white Au and Pd jewellery consists of 85–95 wt% Pd and the balance a mixture of Ga and In in a weight ratio of $\sim 7:3$, with the composition tuned to attain the desired hardness for each application. When used with white Au, the solder may contain the carated amount of Au with the balance a mixture of Pd, Ag, Cu, Zn, Ga and In. The solder melts at ~ 1200 – 1300°C , making it particularly suitable for repair and resizing of Au and Pd jewellery.

ELECTRICAL AND ELECTRONICS

Nanoelectromechanical Switch with Ruthenium Beam

Sandia Corp, *US Patent* 7,719,318 (2010)

A NEM switch is formed on a Si substrate by: suspending a beam of Ru between two anchor points to form the source electrode, **1**; positioning one drain electrode, **2**, or a pair thereof at the midpoint of the beam but laterally offset by a 20–75 nm gap; positioning one or two pairs of electrically-connected gate electrodes, **3**, around the midpoint of the beam but offset by a 30–100 nm gap. The Ru beam is ≤ 10 μm long and ≤ 0.1 μm wide and bows laterally towards **2** in response to an actuation voltage applied across **1** and **3**, thus forming a connection between **1** and **2**. A RuO_2 coating can be applied to **1** to prevent fouling of contact surfaces. The switch can be used to form fast-response NAND and NOR gates or SRAM and DRAM memory cells.



Plasma Display Panels Containing Palladium

Panasonic Corp, *Japanese Appl.* 2010-049,817

A finely-grained pgm powder is included in non-emitting gaps between the front and rear substrates of a plasma display panel, either in the phosphor layer or on the protective layer. The pgm is preferably Pd or Pd alloyed with a transition metal such as Ti, Mn, Zr, Ni, Co, La, Fe or V, and absorbs H₂ released by minor amounts of H₂O and HCs trapped in the panel during construction. It thereby prevents deterioration of the display which occurs over time as the active components react with these contaminants.

ELECTROCHEMISTRY

Improved Anode Catalyst for Chlor-Alkali Cell

Industrie De Nora SpA, *World Appl.* 2010/055,065

An anode has a catalyst layer comprising oxides of Sn, Ru, Ir, Pd and Nb in a molar proportion (based on element) of: 50–70% Sn, 5–20% Ru, 5–20% Ir, 1–10% Pd and 0.5–5% Nb. It is deposited on a valve metal substrate such as Ti or Ti alloy by a multi-coat application of a precursor solution, preferably containing hydroxyacetylchloride complexes of Ru, Ir or Sn; Pd(NO₃)₂ in HNO_{3(aq)} or PdCl₂ in EtOH; and NbCl₅ in BuOH, followed by heat treatment at 400–480°C for 15–30 minutes. The catalyst is highly active for the Cl₂ evolution reaction while maintaining a high overvoltage for O₂ evolution, giving improved cell efficiency.

Iridium-Doped Oxygen Evolution Catalyst

California Institute of Technology, *World Appl.* 2010/045,483

An O₂ evolution catalyst is prepared from a mixture of powders of RuO₂ and a doping metal, M, either Ir or Pb, which is heated at a temperature below the sintering temperatures of both powders so that M is partially oxidised by the RuO₂ to produce MO_xRuO_{2-x} where $x = \sim 0.05$. M may also be present in the catalyst at 5–25 at%, preferably 9–12 at%. The doped Ru oxide catalyst is found to be stable in acidic media and is suitable for use in the anodic oxidation of H₂O in a PEM-based electrolyser.

MEDICAL AND DENTAL

Palladium Coating for Biodegradable Stent

Biotronik SE & Co KG, *US Appl.* 2010/0,161,053

A Pd coating is electrolytically or galvanically applied to an intraluminal endoprosthesis consisting of or containing a biodegradable material, particularly Mg, which releases H₂ as a reaction product while degrading. The Pd layer is preferably 90–100 wt% pure and 2–6 μm thick, with a particle size range of 50–500 nm. It controls the release of H₂ from the stent, so slowing degradation to the desired rate.