

Patents

CATALYSIS – APPLIED AND PHYSICAL ASPECTS

Producing Iridium-Containing Catalysts

Exxonmobil Chemical Patents Inc, *World Appl.* 2011/096,996

A catalyst comprising of Ir dispersed on a support is prepared by: (a) treating a SiO₂-containing support with one Ir compound and one organic compound (e.g. triethanolamine) to form a treated support consisting of an organic Ir complex on the support; (b) heating the treated support in an oxidising atmosphere at ~325–450°C to form a partially decomposed organic Ir complex (this retains 10–95 wt% of the dry weight attributed to the complex before partial decomposition); and (c) heating the treated support in an reducing atmosphere at ~350–500°C to convert the partially decomposed organic Ir complex into the Ir component. The partially decomposed organic Ir complex has one or more IR absorption bands between 2100–2200 cm⁻¹ which were not present in the original organic complex.

Preparation of Tris(dibenzylideneacetone)-dipalladium (chloroform)

Johnson Matthey Plc, *World Appl.* 2011/101,665

The catalyst Pd₂(dba)₃·CHCl₃ is prepared in two steps: (a) a Pd(II) complex (selected from Pd(Hal)₂, Pd(diolefin)(Hal)₂ and Pd(CH₃CN)(Hal)₂) is reacted with an alkali metal halide (Li, Na or K halide) in an alcohol solvent at ~20–50°C; (b) the product obtained from step (a) is reacted with a mixture comprising dba, CHCl₃ and alkali metal acetate over 60 minutes at ~49–53°C to form Pd₂(dba)₃·CHCl₃. The molar ratio of Pd(II) complex:dba is preferably 2:3.20.

Ruthenium-Based Carbene Catalyst

Umicore AG & Co KG, *European Appl.* 2,361,683; 2011

A method for preparing a Hoveyda-type Ru-based carbene catalyst with chelating alkylidene ligands by reacting a Ru alkylidene complex (for example, Ru indenylidene or Ru benzylidene) with an olefin derivative in a cross metathesis reaction in the presence of a polymer-supported cation exchange resin is claimed. The reaction temperature is 20–120°C, preferably in the range of 20–100°C and the reaction time is 0.5–4 h, preferably 0.5–2 h. After the reaction, the solvent(s) are removed, the remaining residues are suspended in a non-polar hydrocarbon solvent, and the precipitated catalyst is separated and dried.

CATALYSIS – REACTIONS

Thermo-Neutral Reforming of Hydrocarbon Fuel

Saudi Arabian Oil Co, *US Patent* 8,008,226; 2011

A multicomponent catalyst consisting of Ni, Ce₂O₃, La₂O₃, Pt, ZrO₂, Rh and Re is used in a thermo-neutral reforming process to produce a H₂-rich synthesis gas from a petroleum-based fuel. The fuel mixture, O₂-rich gas and steam are introduced into an interior zone of a reactor which has a catalyst bed (combined combustion, steam and/or CO₂ reforming catalyst). This mixture is preheated to ~380–450°C and brought into contact with the catalyst bed at GHSV of ~30,000–70,000 h⁻¹ which results in an exothermic reaction (the temperature is raised to ~800–900°C) and causes an endothermic steam reforming reaction for a period of time sufficient to reform the liquid fuel to yield a H₂-rich synthesis gas. The wt% of each constituent of the catalyst is: 0.5–15 Ni; 0.5–10 Ce₂O₃; 0.5–5 La₂O₃; 0.1–2 Pt; 0.5–3 ZrO₂; 0.1–2 Rh; and 0.1–2 Re.

EMISSIONS CONTROL

Platinum-Palladium in Exhaust System

Johnson Matthey Plc, *US Appl.* 2011/0,214,412

An exhaust gas aftertreatment system for a diesel vehicle consists of a NSC followed in a downstream direction by a CSF which has a wall flow filter containing inlet and outlet channels and comprises an oxidative catalyst with an OSC containing CeO₂ or CeO₂-ZrO₂ and a Pd-rich mixture of Pt and Pd. The Pt:Pd weight ratio is < 1:10. The OSC of the oxidative catalyst is 20–50 wt%. A Pt-based oxidative catalyst is situated on the inlet channels and the Pd-rich Pt:Pd oxidative catalyst is located on the outlet channels.

Two Washcoat Layers on a Three-Way Catalyst

BASF Catalysts LLC, *US Appl.* 2011/0,217,216

A catalyst capable of effectively reducing CO in exhaust gas from an internal combustion engine consists of two washcoat layers: (a) a layer comprising of Pd impregnated on a CeO₂-free OSC (for example, ZrO₂-PrO₂) and Pt impregnated on a refractory metal oxide (for example, Al₂O₃); (b) another layer comprising of Pt and Rh impregnated on a CeO₂-containing OSC. The layers consist of 1–90 g ft⁻³ Pt; 1–90 g ft⁻³ Pd and 1–30 g ft⁻³ Rh.

FUEL CELLS

Palladium-Bismuth Catalyst

Univ. Southampton, *British Appl.* 2,478,981; 2011

A catalyst with the composition $Pd_xBi_yM_z$ is used in the anode of a fuel cell and optionally the cathode. M is a metal selected from Pt, Rh, Ir, Os, Ru, Re, Ni, Ag and Au or a combination; $x = 0.1-0.7$; $y = 0.3-0.9$; $z < 0.1$; and $x + y + z = 1$.

Hydrogen Production Apparatus

JX Nippon Oil & Energy Corp, *Japanese Appl.* 2011-088,778

A H_2 production apparatus includes a reforming section which carries out steam reforming of raw materials needed for H_2 production. This part consists of a catalyst comprising of Pt, Pd and Rh on an Al_2O_3 -containing support. The ratio of pgm on the support is 0.3–5:100 wt%. The Al_2O_3 -containing support comprises of $\alpha-Al_2O_3$ which has a pore volume of ≥ 50 nm and the diameter is $0.2-1.0$ ml g^{-1} , carrying 2–25 wt% of rare earth oxides and 0.1–15 wt% of alkaline earth oxides.

METALLURGY AND MATERIALS

Osmium in a Series of Penetrator Rods

J. Wisotzki, *US Appl.* 2011/0,189,325

A single crystal rod is made of an alloy of 40 wt% W, 40 wt% Ti and 20 wt% Os and is grown to the final usable shape in a support free float zoning process. The internal arrangement and control of the support free float zoning process consists of producing single crystal rods in a serial process; necking the intervals between each grown rod down to a diameter of 1.0 mm and separating the grown rods from each other. Compressed rods can be produced by obtaining a powder of high purity W, Ti and Os and compressing this with a die to reduce the O_2 content between the granules of the powder. The single crystal penetrator rods do not break upon impact on a target and enable a size and weight reduction as no material is lost upon impact on the target.

APPARATUS AND TECHNIQUE

Surface-Enhanced Raman Scattering Substrate

Instytut Chemii Organicznej, *European Appl.* 2,369,327; 2011

A substrate for SERS consists of a semiconductor surface (GaN) containing whiskers which are coated with metal or alloy selected from Pt, Ag, Au or Cu.

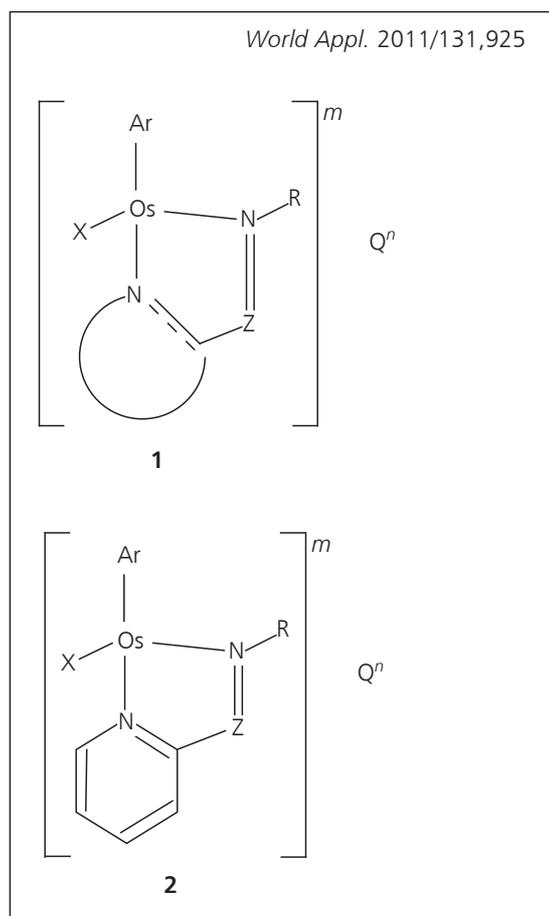
Each whisker contains a linear defect which may be a dislocation or an inversion domain and are connected with each other through terminals, forming conical bunches. The film thickness is 50–150 nm, length of the whiskers range from 0.2–2.0 μm , preferably 0.5–1.5 μm and the diameter ranges from 40–150 nm, preferably 50–70 nm.

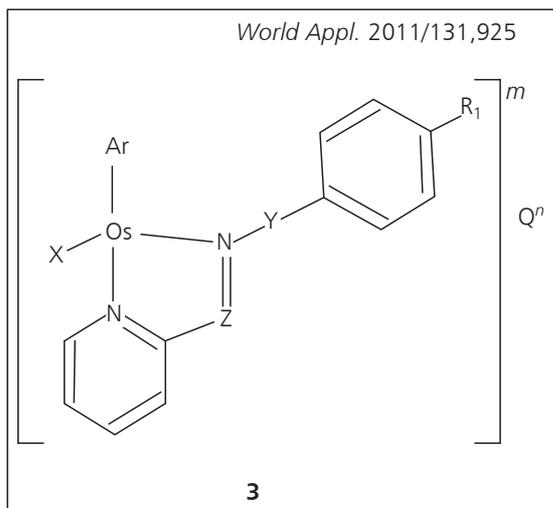
MEDICAL AND DENTAL

Osmium(II) Arene Azo Anticancer Complexes

Univ. Warwick, *World Appl.* 2011/131,925

The Os-containing complexes, **1–3**, can be used as cytotoxic agents, especially as anticancer or immunosuppression agents. Ar is an arene moiety; X is a halo or a donor ligand; Y represents a cyclic or bicyclic ring structure such as a 3, 4, 5, 6, 7 or 8 membered saturated or unsaturated heterocyclic ring; Z is N or CR' ($R' = H, CN, N_3, C_1-C_{10}$ alkyl or aryl); R is a substituted or unsubstituted cyclic or heterocyclic ring; R_1 is H, C_1-C_4 alkyl, OH, amino or substituted amino; Q is an ion which may be present or absent; and m and n are





charges. In **3**, Y is absent or is a C(R')(R'') group. These compounds can be prepared by reacting [ArOsX₂]₂ with an azo or imino containing ligand such as azopyridine or iminopyridine.

Palladium-Based Dental Alloy

DeguDent GmbH, *US Appl.* 2011/0,236,254

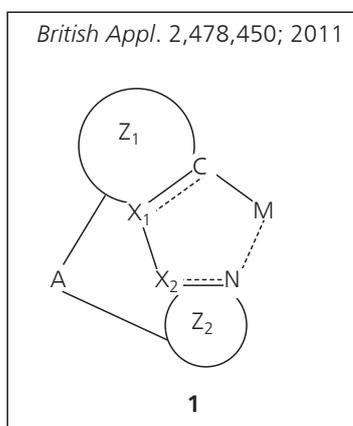
A Pd dominated dental alloy comprises of Au, Pd and Ag, one grain-growth inhibitor (Ru) and a grain-refinement control element (Ta, Nb or a mixture). The dental alloy contains (in wt%): 30–45 Au; 35–50 Pd; 10–25 Ag; 6–10 Sn; 0.03–1.0 Ru; and 0.03–2.0 grain-refinement control element.

PHOTOCONVERSION

Bridged Ring Metal Complexes

Sumitomo Chemical Co Ltd, *British Appl.* 2,478,450; 2011

An electroluminescent metal complex, **1**, where X₁ = C and X₂ = C or N; M = Pt, Pd, Rh, Ir, Os or Ru; and A



represents a group such as an amine or silyl group is claimed. Z₁ and Z₂ represent an optionally substituted aromatic hydrocarbon or heteroaromatic ring. The sum of squares of orbital coefficients of the outermost *d* orbital of M is ≥ 33.3%. The dihedral angle is 9–16°. The complex can be used in a light-emitting device or solar battery.

REFINING AND RECOVERY

Purification of Rhodium-Containing Solutions

Mitsubishi Mater. Corp, *Japanese Appl.* 2011-093,748

The purification of Rh-containing solution (which also contains NH₄⁺ ions) involves adding NO₂⁻ to form a solution containing Rh nitrite complex. The purification process involves: (a) changing the pH to ≥ 1 by adding the NO₂⁻ salt and stirring the solution for ≥ 1 hour at 40°C and pH ≤ 7 for gradually generating Rh nitrite complex ions and decomposing NH₄⁺ ions; (b) heating the solutions to ≥ 70°C and stirring for ≥ 1 h; and (c) solid-liquid separation to recover the precipitated free Rh nitrite complex ion solutions. (NH₄)₃Rh(NO₂)₆ may be generated by the addition of NH₄⁺ salts to the recovered Rh nitrite complex ion solution. Rh recovery yield is improved using this process.