doi:10.1595/147106710X513301

Patents

CATALYSIS – INDUSTRIAL PROCESS

Ruthenium Addition to Nickel Catalyst

Johnson Matthey Plc, *World Appl.* 2010/018,405

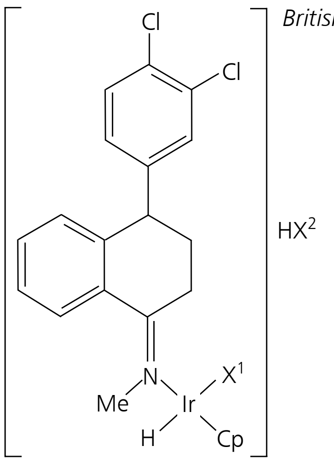
A catalyst for hydrogenation and dehydrogenation reactions containing Ru and Ni in a molar ratio of $(0.15 \times 10^{-3})-0.06{:}1$ exhibits superior resistance to deactivation by acidic components in a feedstream compared to standard Ni-only catalysts. A preferred composition is 10–40 wt% Ni and 0.05–0.25 wt% Ru, with the remainder a porous transition alumina support. It can specifically be applied to the hydrogenation of carbonyl compounds such as butan-2-one and *n*-butyraldehyde in a feedstream containing acidic compounds such as ≤1 wt% of a carboxylic acid.

Iridium Catalyst for High-Yield Sertraline Production

NPIL Pharmaceuticals (UK) Ltd, *British Appl.* 2,464,101 (2010)

A dynamic thermodynamic resolution process for therapeutically active chiral amines such as sertraline consists of: (a) racemising a mixture of amine isomers in solution using an Ir catalyst 1; (b) adding a chiral resolving agent such as mandelic acid to allow selective crystallisation and removal of the desired isomer; and (c) returning the unwanted isomers to step (a). The catalyst may be recovered and recycled through reaction of $NH_{3(g)}$ with 1 to form a solid complex.

British Appl. 2,464,101



1

X^1, X^2 = I, Cl or Br; preferably $X^1 = X^2$ = I
Cp = cyclopentadienyl group optionally substituted by 1–5 independently selected hydrocarbyl substituents; preferably pentamethylcyclopentadienyl

Rhodium-Catalysed Production of Formic Acid

Schlumberger Holdings Ltd, *British Appl.* 2,464,710 (2010)

Formic acid can be produced from CO_2 and H_2 at ≤80ºC using a Rh catalyst containing a nitrosyl ligand, a bidentate organophosphorus ligand, preferably 1,2-bis(dicyclohexylphosphino)ethane (dcpe), and a halogen, preferably Cl. The catalyst is preferably $[Rh(NO)(dcpe)]Cl_2$ and TON is typically >100. The process is carried out in the presence of an organonitrogen base, specifically 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU), which may also act as solvent, or an additional solvent such as toluene or acetone can be used.

EMISSIONS CONTROL

NOx Storage and Reduction with Enhanced Sulfur Tolerance

Honda Motor Co, Ltd, *European Appl.* 2,153,896 (2010)

A NOx treatment system suitable for low- to mid-temperature operation has a first layer with: 0.1–20 g l^{-1} Pt and optionally Rh; 1–100 g l^{-1} La and/or oxides of La, which impart increased resistance to S poisoning; Ce and/or oxides of Ce; and optionally a heat-resistant inorganic oxide. A second component containing a solid acid is either formed as a second layer or mixed with the first. During rich conditions, stored NOx is reduced by CO, HC or H_2, producing N_2, NH_3 and H_2O. The second layer then adsorbs the NH_3, releasing it as a NOx reductant under lean conditions.

Platinum-Palladium Catalyst for H_2-SCR of NOx

Linde AG, *US Appl.* 2010/0,092,360

A catalyst has 0.01–2.0 wt% of each of Pt and Pd, preferably 0.1 wt% Pt and 0.05 wt% Pd, on a nanocrystalline support of 50 wt% MgO and 50 wt% CeO_2. It is formed by wet impregnation from suitable precursors to give highly-dispersed Pt and Pd particles <2 nm in size, and may also have Pt-Pd alloy and oxides of Pt and Pd formed during preparation, calcination or reaction. The catalyst is described to have high activity (>70% conversion of NO) and >80% selectivity to N_2 in the SCR of NOx using H_2 as reducing agent, at low temperatures (100–400ºC) and in the presence of 2–10 vol% O_2, making it ideal for stationary industrial applications.

FUEL CELLS

Controlled Synthesis of Platinum-Cobalt Nanoparticles

Honda Motor Co, Ltd, *World Appl.* 2010/014,500

Pt-Co nanoparticles for cathode catalysts are prepared by heating a mixture of: (a) a Pt precursor such as $Pt(acac)_2$; (b) a Co precursor such as $Co_2(CO)_8$; (c) a capping component, preferably oleic acid and/or oleylamine; and optionally (d) a reducing agent such as 1,2-hexadecanediol. Particle size is controlled by varying the concentration of (c) relative to the total concentration of (a) + (b). Particles ~1–5 nm in diameter are formed in the presence of solvent and particles ~6–12 nm in size are formed in its absence.

APPARATUS AND TECHNIQUE

Durable Palladium Membrane

NGK Insulators Ltd, *European Appl.* 2,156,883 (2010)

A 0.1–10 μm-thick Pd membrane and its use in a selectively permeable membrane reactor for H_2 production is claimed. Membrane composition is 40–90 wt% Pd with added metals A and B, independently selected from: Rh, Ir, Ag, Au, Co, Ni, Cu such that: A and B each form a complete solid solution with Pd, the A-B phase diagram has a triple point, and A and B do not form an intermetallic compound.

Platinum-Catalysed Hydropyrolysis of Steroids for Facilitated Detection

Imperial Innovations Ltd, *European Appl.* 2,157,434 (2010)

A mass spectrometry method for reliably measuring the ratio of ^{13}C to ^{12}C, indicative of natural or synthetic origin of a compound present in a urine sample for example, involves first hydropyrolysis at <350ºC in the presence of a catalyst selected from Pt, Pd, Rh or Ir, preferably Pt. The catalyst may be metallic or deposited at 1–20 wt% on a support which also adsorbs the products of hydropyrolysis. These products are fully deconjugated and can be purified by gas chromatography without the need for further derivatisation.

Iridium Vessel for Melting X-Ray Opaque Glass

Schott AG, *US Patent* 7,687,418 (2010)

A process for preparing a novel, high-melting glass composition is claimed, using a melting vessel of solid Ir or Ir alloy (preferably ≥95 wt% Ir) and heating by high-frequency electromagnetic radiation (50 kHz to 2 MHz) to achieve melting temperatures of ≥1500ºC (preferably ≥1600ºC). The glass, which can be used in dental restorations, contains 0.1–25 mol% Yb_2O_3, rendering it X-ray opaque and therefore suitable for use with imaging techniques.

ELECTRICAL AND ELECTRONICS

Reflective Mask with Ruthenium-Niobium Layer

Hoya Corp, *US Appl.* 2010/0,084,375

A reflective mask blank for use in extreme UV lithography (EUVL) contains a 0.8–5.0 nm-thick RuNb protective film between the multilayer reflective film and the buffer film. For optimal chemical resistance, the RuNb compound is preferably 70–85 at% Ru and 15–30 at% Nb. During patterning of the buffer film using an etching gas containing O_2 and optionally Cl_2, an oxidised layer containing predominantly Nb forms on the protective film and prevents etching damage to the reflective film.

Lead-Free Thick-film Resistor Paste

Sumitomo Metal Mining Co, Ltd, *Japanese Appl.* 2010-015,844

A $BaIrO_3$ conductive powder suitable for use in a resistive paste with Pb-free glass frit and an organic medium or vehicle is prepared by: (a) calcining a precursor such as $(NH_4)_2IrCl_6$ to yield IrO_2; (b) calcining the IrO_2 powder with $BaCO_3$, $BaNO_3$ and/or BaO powder at 650–1000ºC in air to produce $BaIrO_3$; (c) grinding the $BaIrO_3$ to give particles with 20–100 nm mean diameter; and (d) calcining again at 400–650ºC in air to adjust mean diameter to 40–100 nm for ideal, low-noise resistivity characteristics.

ELECTROCHEMISTRY

Lithium-Ion Battery Anode Grown on Platinum Substrate

Toyota Motor Corp, *Japanese Appl.* 2009-295,514

An anode for a rechargeable Li-ion battery is formed by vertically orientating the (003) plane of a $LiCoO_2$ single crystal on the (110) plane of a single crystal metal substrate, either Pt or Au. The lattice spacing of the substrate is close enough to that of the $LiCoO_2$ to allow the film to be grown epitaxially by pulsed laser deposition. This formulation is described as faciliating migration of Li^+ ions within the anode, potentially allowing easier recharging and higher power output.

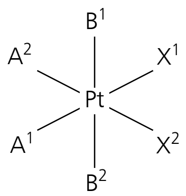
MEDICAL AND DENTAL

Targeted Delivery of Platinum(IV) Anticancer Complex

PLIVA-Lachema as, *US Patent* 7,655,697 (2010)

A pharmaceutical composition has a Pt(IV) anticancer compound, 1, mixed with protective excipients such as saccharides or peptides and optionally a lubricant or disintegrant, contained in a tablet or capsule for oral administration. The capsule is coated with a biodegradable layer and/or a pH-sensitive layer formulated to dissolve in the colon, allowing effective delivery of 1 to the site of colorectal carcinoma in doses of 5–500 mg, preferably 50–350 mg.

US Patent 7,655,697



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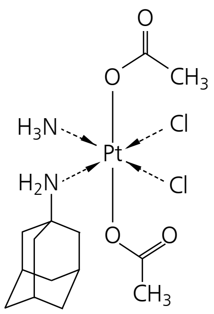


1a

A^1, A^2 = $-NH_3$ or C_1–C_{18} amino group

B^1, B^2 = halogen, hydroxy or –O–C(O)–R; where R = H, alkyl, alkenyl, aryl, aralkyl, alkylamino, C_1–C_{10} alkoxy group or a functional derivative of one of these

X^1, X^2 = halogen or a C_1–C_{20} monocarboxylate group; or X^1 and X^2 together form a C_1–C_{20} dicarboxylate group

An example is shown (**1a**)

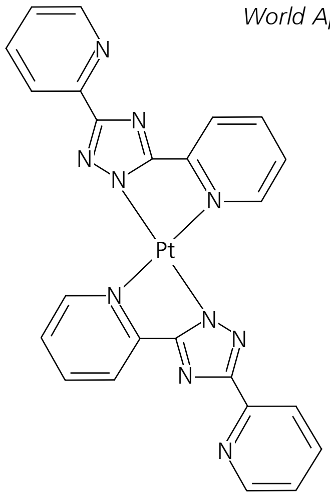
PHOTOCONVERSION

Homoleptic Platinum Complex for WOLEDs

Univ. North Texas, *World Appl.* 2010/016,990

Square planar complexes M(N^N)$_2$, where M is Pt, Pd or Ni and N^N is a bidentate anionic ligand, preferably a triazolate, are claimed for use in the emissive layers of OLEDs, particularly white OLEDs (WOLEDs), and as the n-type material in organic thin film transistors used in complementary metal-oxide-semiconductor (CMOS) devices. A preferred complex, 1, has excellent colour stability even at high luminance and superior photoluminescent properties, allowing improved efficiency in these devices.

World Appl. 2010/016,990



1 Bis[3,5-bis(2-pyridyl)-1,2,4-triazolato]platinum(II)

Iridium-Doped Phosphor

Kuraray Luminas Co, Ltd, *US Appl.* 2010/0,032,628

A phosphor is produced by firing a Group 12–Group 16 compound semiconductor such as ZnS, ZnSe, CdS or CdSe with an Ir compound such as $IrCl_3$, $(NH_4)_2IrCl_6$ or $(NH_4)_2IrBr_6$, and optionally S and a flux. Firing is preferably accomplished using a ≥0.1 GPa shock wave to rapidly heat the mixture to reaction temperature, with subsequent rapid cooling, to allow Ir to disperse uniformly in the phosphor for optimal efficiency. Ir content is preferably 10–8,000 ppm, with the amounts of Ir contained within the phosphor and on the surface not varying by more than 5% relative to each other.

REFINING AND RECOVERY

Reuse of Ruthenium from Manufacturing Waste

Air Liquide, *World Appl.* 2009/122,240

Recovery and purification of RuO_4, used as a precursor in the manufacture of semiconductor devices, is accomplished by: (a) heating the gaseous waste stream in a vessel at 50–800ºC and 0.01–1000 torr, optionally in the presence of a Ru or RuO_2 catalyst, to convert the RuO_4 to a lower oxide in solid form; (b) reducing this with H_2 to Ru metal with a specific surface area of >1.0 $m^2\ g^{-1}$, preferably ~7.0 $m^2\ g^{-1}$; (c) oxidising the metallic Ru using at least one of NO, NO_2, O_2, O_3 or plasmas thereof to give RuO_4; and (d) purifying this secondary stream to ≥99.9% RuO_4 through distillation for reuse.