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 \(\leq 1\%\) of a carboxylic acid.

Iridium Catalyst for High-Yield Sertraline Production
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; (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 \(\text{NH}_3(\text{g})\) with \(1\) to form a solid complex.

Rhodium-Catalysed Production of Formic Acid
Schlumberger Holdings Ltd, British Appl. 2,464,710 (2010)
Formic acid can be produced from \(\text{CO}_2\) and \(\text{H}_2\) at \(\leq 80^\circ\text{C}\) 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
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 \(\text{H}_2\), producing \(\text{N}_2\), \(\text{NH}_3\) and \(\text{H}_2\text{O}\). The second layer then adsorbs the \(\text{NH}_3\), releasing it as a NOx reductant under lean conditions.

Platinum-Palladium Catalyst for \(\text{H}_2\) 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 \(\text{N}_2\) in the SCR of NOx using \(\text{H}_2\) as reducing agent, at low temperatures (100–400\(^\circ\text{C}\)) and in the presence of 2–10 vol% \(\text{O}_2\), 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
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$_2$O$_3$, 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$_4$)$_2$IrCl$_6$ to yield IrO$_2$; (b) calcining the IrO$_2$ powder with BaCO$_3$, Ba(NO$_3$)$_2$ and/or BaO powder at 650–1000ºC in air to produce BaO$_3$Ir; (c) grinding the BaO$_3$Ir 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 facilitating 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*


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](image)

**PHOTOCONVERSION**

*Homoleptic Platinum Complex for WOLEDs*


Square planar complexes \(M(N^N)^2\), where \(M = Pt, Pd\) or \(Ni\) and \(N^N\) is a bidentate anionic ligand, preferably a triazole, 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.

![Homoleptic Platinum Complex for WOLEDs](image)

**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 50–800°C 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.