

NEW PATENTS

ELECTROCHEMISTRY

Cermet Electrodes for Oxygen Reduction

ROBERT BOSCH GmbH *European Appl.* 1,303,753

Pt-cermet electrodes, used for the electrochemical reduction of O_2 , have a ceramic portion containing stabilised ZrO_2 as the main component. The composition of the electrodes is designed to reduce their polarisation resistance.

Rhodium Sulfide Electrocatalyst

DE NORA ELETTRODI SPA *World Appl.* 03/040,435

A Rh sulfide electrocatalyst (1) for reduction of O_2 in industrial electrolyzers is produced by heating an aqueous solution of a Rh salt to obtain a steady distribution of isomers and then sparging H_2S into the solution. (1) is supported on highly dispersed C black and is highly resistant towards corrosion and poisoning by organic species. Thus (1) is particularly suitable for use in aqueous HCl electrolysis, even when in an acid containing organic contaminants. The activity and consistency of (1) is substantially improved.

Low-Sulfur Platinum Aluminide Layers

GENERAL ELECTRIC CO *U.S. Patent* 6,551,423

A method for preparing coated Ni-base superalloy, used in high-temperature applications, lowers the S content of the surface of the metallic coating layers. This improves the adhesion of the coating layers to the article. A first layer, of Pt, is deposited to overlay the surface of a substrate, followed by a second layer, of Al, over the Pt. The article is desulfurised by heating in H_2 , and a small amount of surface material exposed during the heating is removed. A ceramic layer may be deposited over the desulfurised article.

APPARATUS AND TECHNIQUE

Spark Plug with Yttrium-Stabilised Platinum Alloy

FEDERAL-MOGUL CORP *European Appl.* 1,312,144

A spark plug with ground and centre electrodes includes a firing tip (1) formed from an alloy containing Pt, W and Y oxide. (1) can be a pad, a rivet, a ball or wire, etc., and can be welded in place on the electrode. (1) gives good erosion resistance, a reduced spark voltage, good welding and forming characteristics, as well as a minimal occurrence of alloy oxidation at the weld area.

Iridium Ultramicroelectrode Array

TRUSTEES OF TUFTS COLLEGE *U.S. Patent* 6,527,930

An Ir ultramicroelectrode (1) includes: a Si substrate; a Si oxide insulating layer; a Ti adhesion layer; and an Ir layer deposited over and insulated from the substrate. Part of the Ir surface (the ultramicroelectrode) is exposed. Also included are: a Au bond pad layer; a Ti adhesion layer; and a SiO_2 insulating layer. Preferably, (1) does not include Hg. (1) and devices using (1) can determine levels of Cu^{2+} or Hg^{2+} using square wave anodic stripping voltammetry.

Catalytic Removal of Oxygen from Sealed Packages

JOHNSON MATTHEY PLC *U.S. Patent* 6,562,258

Small quantities of entrained O_2 are removed from sealed packages containing an oxidisable product, such as a perishable foodstuff, using a particulate catalyst (1) with high activity for combining H_2 and O_2 . (1) can be a Pt group metal supported on a porous inert carrier with the particles being partially encapsulated on a surface of a H_2O -insoluble adhesive on an inside surface of the sealed package. The adhesive material can be poly(vinylbutyral), nitrocellulose, ethyl cellulose, a polyurethane or a Si rubber.

HETEROGENEOUS CATALYSIS

Highly Selective Shell Impregnated Catalyst

SAUDI BASIC IND. CORP *European Appl.* 1,303,471

A highly selective shell impregnated Pd-Au catalyst (1) on a SiO_2 support, with improved space time yield (STY) for vinyl acetate (VA) production, has a Pd loading of $1.8-7.2 \text{ g l}^{-1}$ and a Au:Pd weight ratio of 0.3:2.0. The support can be further impregnated with K acetate. At $140-160^\circ\text{C}$ and a gas hourly space velocity of 4500 h^{-1} at 120 psig, (1) has VA selectivity of $\geq 90\%$ when operated under a STY of ≥ 600 .

Aluminium-Modified Palladium/Carbon Catalyst

COUNCIL SCI. IND. RES. *European Appl.* 1,308,206

A highly active Al-modified C-supported Pd catalyst (1) is prepared by simultaneously impregnating activated C with 2-6 wt.% Pd precursor and 1-50 wt.% Al precursor both with respect to the C support. (1) is useful for the hydrodechlorination of dichlorodifluoromethane to produce difluoromethane with 85% conversion rate at atmospheric pressure.

Eliminating NOx by a Laminated Structure

INST. FRANCAIS DU PETROLE *World Appl.* 03/009,918

Material (1) comprising mixed oxides with metals in octahedral coordination are linked to make a laminated structure. (1) are used to remove NO and NO_2 from ICE exhaust gas. (1) contains Mn, W, Zr, etc.; Al, Zn, Cd, etc.; and Pt, Pt-Rh, Pd-Rh, etc.; supported on SiO_2 , Al_2O_3 , etc. The ICE operates in a medium containing oxidants above stoichiometric level, and NO_x can be adsorbed and later desorbed by a temperature rise. Pt metals with (1) can eliminate NO_x adsorbed by reduction in a rich mixture.

Low Surface Acidity Catalysts

JOHNSON MATTHEY PLC *World Appl.* 03/013,728

A catalyst (1) suitable for the dehydrogenation and hydrogenation of hydrocarbons comprises a first metal of a Pt group metal(s) and a second metal comprising Sn, Ge, Pb, etc., bound to a support material. The support, containing Al_2O_3 , spinel, SiO_2 , etc., has an overlayer to block acidic sites on the support. (1) is also substantially chloride free. A preparation method for (1), that uses $K_2[Pt(C_2O_4)_3]$ and $Sn(BF_4)_2$ precursors in citric acid solution, is also disclosed.

High-Activity Isomerisation Catalyst

UOP LLC *World Appl.* 03/020,420

A catalyst and process is disclosed to selectively upgrade a paraffinic feedstock to an isoparaffin-rich product for blending into gasoline. The catalyst comprises at least one Pt group metal component, preferably Pt, on a support of a sulfated oxide or hydroxide of a Group IVB (IUPAC 4) metal, and a lanthanide element or an Y component, preferably Yb.

Exhaust System with Hydrocarbon SCR Catalyst

JOHNSON MATTHEY PLC *World Appl.* 03/033,118

Exhaust gas in an ICE containing NO_x and hydrocarbons is reduced in an exhaust system that comprises two hydrocarbon selective catalytic reduction (HC-SCR) catalysts. The first HC-SCR catalyst contains a transition metal on a support selected from Al₂O₃, TiO₂, ZrO₂ or non-zeolite SiO₂-Al₂O₃, etc. The second Pt-based HC-SCR catalyst is placed with and/or downstream of the first HC-SCR catalyst, wherein the exhaust system has means for coking the catalyst during normal engine operation.

Exhaust Line for an ICE

JOHNSON MATTHEY PLC *World Appl.* 03/037,507

An exhaust system for an ICE comprises a catalysed particulate filter (1) having a NO_x absorbent, such as an alkali metal, an alkaline earth metal and a rare earth metal, capable of absorbing NO_x in an exhaust gas (2) when its composition is $\lambda > 1$, and capable of releasing the NO_x absorbed in the NO_x component when the composition of (2) is $1 \geq \lambda$. (1) further comprises a Pt and/or Pd oxidation catalyst and Rh capable of oxidising NO to NO₂ when the air:fuel ratio of (2) is lean.

Double Bond Hydrogenation in Unsaturated Carbonyls

CHEMI SPA *World Appl.* 03/037,508

A process is described for preparing a Rh-based catalytic system (1) heterogenised on an organic or mineral support. It involves the reduction of a Rh derivative with a valency state > 0 in an ether or aromatic solvent and in the presence of a compound chosen from the group consisting of lipophilic tertiary amines, lipophilic tertiary amides and lipophilic quaternary ammonium salts. The mixture obtained is adsorbed onto a suitable organic or mineral support. (1) is used in the hydrogenation of a C=C double bond of an α,β -unsaturated carbonyl compound.

Tin Promoted Iridium Carbonylation Catalyst

EASTMAN CHEMICAL CO *U.S. Patent* 6,548,444

A carbonylation catalyst (1) contains a solid component with 0.1–10 wt.% Ir and 0.1–10 wt.% Sn in contact with an activated C catalyst support, and a vaporous halide component selected from HI, MeI, etc. (1) is used for producing esters and carboxylic acids from reactants including lower alkyl alcohols, lower alkyl alcohol generating compounds, such as ether and ester derivatives of the alcohols, and their mixtures in a vapour phase carbonylation process.

Hydrogenated Polymers

KURARAY CO LTD *U.S. Patent* 6,559,241

A hydrogenated polymer is prepared from a polymer having C=C bonds and a hydroxy group and/or a functional group, which is convertible into a hydroxy group or into a hydroxymethyl group, in the presence of a Pd and/or Pt catalyst supported on a base activated C (1). (1) is prepared by treating an activated C with a base and depositing on it a Pd or Pt salt, which is converted to metal by hydrogenation. (1) removes the sites of unsaturation in the polymer and thus improves the low heat resistance and weatherability of the polymer.

Conversion to Hydrogenated Fullerenes

NATL. INST. ADV. IND. TECHNOL.

Japanese Appl. 2003/012,572

The conversion of a fullerene comprises converting C₆₀ fullerene to a hydrogenated fullerene (1) using a catalyst obtained by impregnating Ru, Pd, Ir, Pt or Co into an active Al₂O₃. Conversion of the fullerene to C₆₀H₁₈ or C₆₀H₃₆ occurs in high efficiency under mild hydrogenation conditions. The method allows efficient production of (1) as a H storage material.

Carboxylic Acid Ester Production

ASAHI KASEI CORP *Japanese Appl.* 2003/024,782

A catalyst (1) for producing a carboxylic acid ester (2) from an aldehyde, an alcohol, and O₂ comprises Pd/active C. The Pd is supported on an active C carrier that has specific surface area 500–1500 m². The particle size of the carrier is 75–600 mesh, the bulk density is 0.3–0.8 g ml⁻¹, and the Pd has specific surface area of ≥ 50 m² g⁻¹. (1) has high reactivity and (2) is produced at lower cost.

HOMOGENEOUS CATALYSIS

Ruthenium Complexes Containing Carboids

BASF AG

European Appl. 1,311,520

Ru carboid-containing complexes, used as catalysts in metathesis polymerisation reactions (ROMP, ADMET, etc.) of olefins comprise: H or optionally substituted C1–20 alkyl, C6–20 aryl or C7–20 alkyl-aryl radicals; and independent neutral electron donor ligands coordinated at the Ru centre as carboids and which can be linked by a bridge W with 0–20 C atoms. The bridge can be a constituent of a cyclic or aromatic group and can be split by heteroatoms, except C,N-heterocyclic five-membered ring systems.

Infusion of Cyclic Olefin Resins into Porous Materials

MATERIA INC

World Appl. 03/020,504

Compositions are claimed comprising porous materials infused with polymers obtained from metathesis reactions, for example, ROMP derived polymers and ADMET derived polymers. Cyclic olefin monomers, including Ru or Os carbene metathesis catalysts, are useful to infuse the porous materials. A method for preparing the porous materials infused with the cyclic olefin resin formulations is described.

Improvements Relating to Prostaglandins

JOHNSON MATTHEY PLC *World Appl.* 03/037,857

A selective reduction of the 13, 14-double bond (in the presence of the 5, 6-double bond and unprotected hydroxyl groups) of certain prostaglandin C-1 esters, particularly PGE₂, PGD₂, PGE₂, etc., and their analogues, can be achieved directly by the use of homogeneous catalysts (1). (1) coordinate with the 15-hydroxyl group and selectively deliver up H to the 13, 14-double bond. (1) include Wilkinson's Rh catalyst, Crabtree's Ir catalyst and Evans' Rh catalyst.

Ruthenium Compound Catalysts

CHUBU CHELEST CO *U.S. Patent* 6,548,688

H₂O-soluble diammonium Ru diethylenetriamine-pentaacetates or hydrates are produced. They are excellent in handling and exhibit very high, long-term stability both in air and in aqueous solution. The Ru compounds are useful as catalysts for the synthesis of NH₃, the hydrogenation of carbonyl or aromatic compounds, and as raw material for the production of Ru-base metal oxide ceramics.

Oxidative Carbonylation of Toluene

E. I. DU PONT DE NEMOURS CO *U.S. Patent* 6,548,698

The oxidative carbonylation of toluene, catalysed by Rh or Ir complexes in the presence of an oxidant, such as K₂S₂O₈, H₂O₂, trifluoroperacetic acid, etc., and under mild conditions, produces toluic acid with *para*-selectivity $\leq 98\%$. The Rh compound may be [XRh(CO)₂], where X is an anionic ligand selected from acetylacetonate, trifluoroacetylacetonate, hexafluoroacetylacetonate, etc. The Ir compound may be IrX₃·nH₂O, where $n = 0-10$, and X is an anion selected from F⁻, Cl⁻, Br⁻ and I⁻.

Production of Acyclic Olefins

DEGUSSA AG *U.S. Patent* 6,552,139

Acyclic olefins with two or more C atoms and/or cyclic olefins are prepared using homobimetallic and heterobimetallic alkylidene complexes of Ru containing N-heterocyclic carbene ligands. The Ru complexes also contain: an anionic ligand, a monodentate to tridentate ligand which contains a metal and is nonionically bound to the Ru centre, and radicals which may be identical or different and are each H or/and a hydrocarbon group, but may also form a ring, and the N-heterocyclic carbene ligand.

Mixture of Isomers of Hydrogenated Bisphenol

MARUZEN PETROCHEM CO LTD *Japanese Appl.* 2003/002,853

Mixtures of hydrogenated bisphenol A isomers (1) containing isomers: *cis-cis*, *cis-trans* and 36-45% *trans-trans* forms are produced by subjecting bisphenol A to catalytic hydrogenation using a Ru catalyst in the presence of a solvent (aliphatic alcohol-based and/or glycol ether-based) at 100-130°C, under pressurised H₂. (1) has excellent compatibility with other resin raw materials and paint solvents and is used as raw material for polyester resin-based paints.

1-Boryl-4-stannyl-1,3-diene Compound

JAPAN SCI. TECHNOL. CORP *Japanese Appl.* 2003/026,692

1-Boryl-4-stannyl-1,3-diene compound (1), in which substituted diamino groups are bound to a B atom, is produced by reacting an alkyne compound with a borylstannane compound in the presence of a catalyst comprising Pd and a phosphite ligand. (1) is used as an intermediate for medicines and agrochemicals or as raw material for producing fine chemicals.

FUEL CELLS

Methanol Decomposition Reactor

GENERAL MOTORS CORP *U.S. Patent* 6,541,142

A fuel cell system contains a MeOH decomposition reactor (1) used to solve cold startup and problems with transient operating conditions. A catalyst containing 10-20 wt.% Pd/ZrO₂ is particularly suitable for MeOH low temperature decomposition. MeOH is charged into (1) and heat is supplied to decompose MeOH (endothermic reaction) to H₂ and CO. The H₂ produced is used by the fuel cell stack.

Electrode Structure for Solid Polymer Fuel Cell

HONDA MOTOR CO LTD *Japanese Appl.* 2002/367,629

A polymer electrolyte film (1) for the electrode structure of a SPFC, has repeating units composed of a sulfonated compound of a polyether group of molecular weight 10,000-1,000,000. An electrode catalyst layer contains 0.01-0.6 mg Pt cm⁻², and the average diameter of the C grain is 10-100 nm. (1) has excellent power generating property at reduced cost.

Hydrogen Gas Generation

ULVAC JAPAN LTD *Japanese Appl.* 2003/012,301

A composition for H₂ gas generation is made by diffusing ≥ 0.1 wt.% Al into an Ir-Ga alloy, the alloy being adhered to the Al surface. This is brought into contact with H₂O to produce H₂ gas. The apparatus (1) for H₂ gas production consists of a vessel which houses the alloy and various piping. High purity H₂ gas is obtained from the convenient, lightweight production. By combining (1) and a fuel cell, the generated H₂ gas can be used as the H₂ source.

ELECTRICAL AND ELECTRONIC ENGINEERING

Composite Iridium Barrier with Oxidised Refractory

SHARP LAB. AMERICA INC *U.S. Patent* 6,566,753

An Ir-M-O composite film (1) (M includes a variety of refractory metals), that effectively prevents O₂ diffusion and is resistant to high temperature annealing in O₂, is claimed. When used with an underlying barrier layer of oxidised M transition metals, Ir diffusion into underlying Si substrates is suppressed, and Ir silicides are not formed. (1) remains conductive, not peeling or forming hillocks, during high temperature annealing. Conductive electrode/barrier structures with (1) are useful in nonvolatile MFMIS memory devices, DRAMs, capacitors, pyroelectric IR sensors, etc.