

Homogeneous Hydrogenation of Carbon Monoxide by Iodide-Promoted Ruthenium Catalysts

B. D. DOMBEK, *182nd Am. Chem. Soc. Natl. Meeting*, New York, Aug. 23-28, 1981

A new type of homogeneous Ru catalyst has been developed for hydrogenating CO to methanol, ethanol and free ethylene glycol, where glycol is the major product. The system has basic promoters, such as ionic iodide promoters and polar solvents. Typical promoters include NaI, KI or bis(tri-phenylphosphine)iminium iodide and typical solvents are N-methylpyrrolidone, sulfolane and 18-crown-6. The new system has activity, substantially higher than known Ru catalysts.

Triphenylphosphine Ruthenium(II) Complex with Tin(II) Trichloride and Its Catalytic Properties

P. G. ANTONOV, N. V. BORUNOVA, I. N. KUKUSHKIN and L. KH. FRIEDLIN, *Khim. Khim. Tekhnol.*, 1981, **24**, (6), 663-665

The prepared complex catalyst $[\text{Ru}(\text{PPh}_3)_2(\text{SnCl}_3)\text{Cl}]$ was found to be active during hydrogenation of unsaturated hydrocarbons but was inactive during isomerisation. The rate of olefin and diene hydrogenation was very high. The activity of the catalyst was 4-5 fold higher than that of $[\text{Ru}(\text{PPh}_3)_3\text{Cl}_2]$. The presence of strongly *trans*-orientating SnCl_3 ligands in the sample increased its catalytic activity and also the stereospecificity of diene hydrogenation.

NEW PATENTS

METALS AND ALLOYS

Platinum-Rhodium Alloys

OWENS-CORNING FIBERGLASS CORP.

British Patent 1,597,659

New alloys having low creep rates, suitable for glass fibre production bushings, contain 10-40% Rh, 0.001-0.01% B, 0.015-1.25% Zr, Mg, Y, La, Ti, Hf, Nb and/or Ta and the remainder Pt.

Electroplated Silver-Palladium Contact Materials

BELL TELEPHONE LABORATORIES INC.

U.S. Patent 4,269,671

Pd-Ag alloys, plated from baths containing Li chloride and other Group IA or IIA metal halides, have improved corrosion resistance over similar wrought alloys, allowing larger amounts of Ag to be used in the alloys. Plated Pd-Ag alloys may be used in applications where Au is the normal contact material and the corrosion of the underlying base metal substrate by the plating solution is avoided by Au-flashing the substrate prior to plating.

ELECTRICAL AND ELECTRONIC ENGINEERING

Contact Resistance Measurements of Platinum-Silicide and Chromium Contacts to Highly Doped n and p Silicon

G. BOBERG, L. STOLT, P. A. TOVE and H. NORDE, *Phys. Scr.*, 1981, **24**, (2), 405-407

A comparison of contact resistivity for Pt silicide contacts and sputtered Cr contacts on heavily doped n- and p-Si was made by a method suitable for contacts of a highly conductive surface layer on a less conductive base material. The results showed less spreading and lower specific contact resistance for PtSi contacts on both n⁺ and p⁺-Si, than for Cr contacts which with p⁺ showed non-ohmic behaviour.

Palladium with a Thin Gold Layer as a Sliding Contact Material

T. SATO, Y. MATSUI, M. OKADA, K. MURAKAWA and Z. HENMI, *IEEE Trans. Components, Hybrids, Manuf. Technol.*, 1981, **CHMT-4**, (1), 10-14

Two types of electroplated Pd contacts, one with a thin Au layer, were evaluated as substitutes for Au. The Au deposit properties were as good as acid hard gold deposits. Friction coefficients were 0.4-0.7 for electroplated Pt and 0.15-0.3 for electroplated Au. The multilayer contact had friction properties similar to those of Au contacts, and the Au acted as a lubricant between the harder Pd electroplates. Pd had good results in 1000-hour corrosion tests in an 80%N₂-20%O₂ atmosphere containing 10 ppm H₂S.

ELECTROCHEMISTRY

Water Heater Non-Sacrificial Anodes

RHEEM INTERNATIONAL INC. *British Patent* 1,596,839

A water heater tank is protected from corrosion by means of an impressed current supplied from a Ti-Pt non-sacrificial anode and a Pt or Pd water recombination catalyst fitted at the top of the tank.

Photogalvanic Production of Hydrogen

TOKYO INSTITUTE OF TECHNOLOGY

British Appl. 2,071,154 A

H₂ is produced by irradiating an aqueous solution of alkylammonium salt of polytungstic or polyvanadic acid in a photogalvanic cell having Pt, Pd or W electrodes.

Catalytic Electrode

GENERAL ELECTRIC CO.

British Appl. 2,071,157 A

The use of Ru oxide electrodes for the liberation of halogens by the electrolysis of aqueous halide solutions has not been successful because of attack by the acidic electrolyte. Now, by stabilising the oxides by a

high temperature treatment in the presence of O_2 , these problems are overcome. The treatment may be used with other reduced platinum group metal oxide coatings.

Catalysed Chloralkali Cathode

JOHNSON MATTHEY & CO. LTD.

British Appl. 2,074,190 A

A cathode for use in brine or water electrolysis cells is made from an electrically conductive matrix carrying a surface deposit of a platinum group metal, Au or Ag catalyst, preferably Pt and/or Ru. The matrix may be made of Ni, Cu, austenitic steel or another base metal on to which the catalyst is deposited by chemical displacement. A mild steel cathode body may be plated with Ni, etched and then chemically plated with Pt and Ru. The cathode surface has a roughness factor of 100–500 cm^2/cm^2 .

Electrodes for Electrolysis

OLIN CORP.

European Appl. 39,022

Electrodes which are highly conductive and mechanically strong but require greatly reduced amounts of metal are obtained by plating a textile substrate such as a polyester cloth with a suitable metal which may be a platinum group metal or Au, or their alloys.

Electrochemical Moisture Measuring System

NATIONAL RESEARCH DEVELOPMENT CORP.

U.S. Patent 4,269,683

An electrochemical system for determining the proportion of water in ethanol (or the moisture content of C powder) uses an active electrode containing Pb in contact with its oxide and a counter electrode consisting of Pt, Rh, Ir, Ni or Zr in contact with its oxide. A preferred combination is Pb/PbO₂/PbSO₄ vs. Pt/PtO₂.

Hydrogen and Oxygen Production

KERNFORSCHUNGSANLAGE JULICH G.m.b.H.

U.S. Patent 4,274,938

In an apparatus for the production of H₂ and O₂ by the electrolysis of Na and/or K hydroxide, the H₂ is reacted with Li to form LiH which is subsequently decomposed by heat. The anode is preferably a sheet of Pt and the membrane cathode is a Pd foil coated with Fe on the side towards the Li melt.

ELECTRODEPOSITION AND SURFACE COATINGS

Vapour Coating of Powders

UNISEARCH LTD.

British Appl. 2,074,610 A

Individual particles of a powder may be effectively coated by using an electrostatic field to convert them to a fluidised state and then passing a vapour of the coating material through the dispersion. Pt and Pd catalysts may be deposited on supports by this method.

Palladium-Indium Plating

KHAR'KOVSKIY GOSUDARSTVENNIY PEDAGOGICHESKIY INSTITUT IM. G.S. SKOVORODY

Soviet Patent 834,263

Baths of improved stability for the electrocodeposition of Pd and In contain, per litre, 6–12 g Pd chloride (as metal), 10–20 g In chloride (as metal), 0.5–1.0 g Dy chloride (as metal), 50–120 g Trilon B, 20–40 g NH₄Cl, and 70–120 g NH₄OH.

HETEROGENEOUS CATALYSIS

Enriched Rhodium Catalyst

FORD MOTOR CO. LTD.

British Patent 1,597,291

A catalyst is made from Pt and Rh and is heated in an oxidising atmosphere at 650–875°C for at least two hours so that the ratio of Rh : Pt in the surface becomes greater. Thus the surface of the catalyst is enriched in Rh above the 19 : 1 ratio found in nature. The catalyst is particularly used in automotive exhaust gas treatment.

Preparation of Ethylene Glycol

HOECHST A.G.

British Patent 1,599,598

Glycolic acid can be hydrogenated to ethylene glycol under relatively mild conditions if the catalyst used contains a platinum group metal, especially Pt, Pd and/or Ru, and a Group VIIB and/or IB metal, preferably Re, Au and/or Ag.

Catalytic Combustion

JOHNSON MATTHEY & CO. LTD.

British Patent 1,601,687

The claimed gas turbine allows a major portion of the fuel to undergo catalytic combustion within a chamber having a capacity similar to that of non-catalytic combustion chambers. The catalyst used is preferably a platinum group metal, supported on a monolith preferably formed from a Pt-Rh or a MCrAlY alloy.

Catalytic Decomposition of Ozone

JOHNSON MATTHEY & CO. LTD.

British Appl. 2,056,424 A

O₃ is removed from gases by decomposition to O₂ over a catalyst containing one or more of Pt, Ru, Pd, Ir, Os, Rh, Fe, Co, Ni, Ag, Mn and Sn and/or alloys, mixtures and compounds containing one or more of these metals. Preferably the catalyst metal is deposited on a wash-coated metal alloy support.

Oxidation of Methanol

JOHNSON MATTHEY & CO. LTD.

British Appl. 2,069,366 A

A cheaper and more active catalyst or catalyst support is made by melt spinning or melt extraction from metals and/or alloys of platinum group metals Ag and/or Au. The catalyst bodies may be used for exhaust gas treatment, formaldehyde production from methanol and isopropanol dehydrogenation. Melt spun 0.1% Pt-Ag and 0.5% Au-Ag are used in examples of methanol oxidation.

Food Treatment

JOHNSON MATTHEY & CO. LTD.

British Appl. 2,074,889 A

O₂-containing gas and a fuel are passed over one or more catalysts to heat the gas stream. Platinum group metal catalysts on monolithic supports are preferably used. The heated gas stream is contacted with foodstuffs which are to be heated.

Catalysts

UNISEARCH LTD.

European Appl. 32,455

Catalysts having a wide range of activity are obtained by grafting a monomer, such as styryl diphenyl phosphine on to a metal or polymer substrate under the action of u.v. or ionising radiation and reacting this support with a platinum group metal complex, such as (PPh₃)₃Ir(CO)Cl or (PPh₃)₃RhCl.

Hydrocarbon Reforming

EXXON RESEARCH & ENGINEERING CO.

European Appl. 36,048

An improved start-up procedure for a hydrocarbon reforming process involves sulphiding the catalyst which preferably consists of bimetallic clusters of Pt and Ir dispersed on an inorganic oxide support.

Hydrophobic Recombination Catalyst

VARTA BATTERIE A.G.

European Appl. 37,953

H₂ and O₂ formed during battery charging are recombined over a catalyst formed from a PTFE-kieselguhr mixture, impregnated with Pd chloride solution, coated with a PTFE emulsion and then baked at 430°C.

Noble Metal Zeolite Catalyst for Xylene Isomerisation

MOBIL OIL CORP.

European Appl. 38,141

Pt, Pd, Rh, Ir, Os, Ru, Ag or Au, in cationic form is added to a zeolite of the ZMS type prior to final particle formation, to produce an active catalyst for xylene isomerisation.

Catalytic Hydrogenation of Nitrobenzene

BAYER A.G.

U.S. Patent 4,265,834

A highly active, low cost, long life catalyst for the production of aniline contains 1–20 g/l of a noble metal, preferably Pd, and 1–20 g/l of a further non-noble transition metal supported on Al₂O₃ having a specified BET surface area.

Production of High Octane, Lead-Free Petrol

INSTITUT FRANCAIS DU PETROLE

U.S. Patent 4,268,701

The petrol is obtained by a combination of steps which include oligomerisation of the 3C cut, hydroisomerisation of 1-butylene in the 4C cut in the presence of a Pd or other platinum group metal catalyst, fractionation of the resultant 4C cut, hydrogenation of isobutylene (for instance in the presence of a Pt or Pd catalyst) and alkylation.

Oil Hydrogenation Catalysts

LEVER BROTHERS CO.

U.S. Patent 4,278,609

The selectivity of hydrogenation of the polyunsaturated fatty acid triglycerides in natural oils is increased by pretreating the C-supported Pt, Pd, Rh or Ir catalyst with NH₃.

Spheroidal Alumina Catalyst Supports

W. R. GRACE & CO.

U.S. Patent 4,279,779

Spheroidal catalyst supports prepared by an improved external gelation oil-drop process have high surface area, good crush strength and excellent attrition resistance. When impregnated with platinum metals the supports produce highly active, long life I.C.E. exhaust purification catalysts.

Production of Hydrogen Peroxide

TOKUYAMA SODA K.K.

U.S. Patent 4,279,883

High yields of H₂O₂ are obtained from the direct reaction of H₂ and O₂ when the reaction is carried out in an aqueous solution containing dissolved H₂ in the presence of a platinum group metal catalyst, especially Ru, Pd and/or Pt, containing adsorbed H₂.

Palladium Dehydrogenation Catalyst

W. C. HERAEUS G.M.B.H.

German Offen. 3,000,857

A catalyst for the oxidative dehydrogenation of cyclohexene to benzene consists of an Al₂O₃ carrier supporting 0.1% Na and 0.5% Pd.

HOMOGENEOUS CATALYSIS

ABS Polymer Hydrogenation

JOHNSON MATTHEY & CO. LTD.

British Appl. 2,070,023 A

The hydrogenation of an unsaturated organic material by contact with gaseous or dissolved H₂ is enhanced by using the material in the form of an emulsion. Suitable catalysts are Rh-phosphine, arsine or stibine complexes, such as (Ph₃P)₃RhCl. Using this method the susceptibility of certain polymers to oxidative degradation is contained.

Rhodium-Tertiary Phosphine Hydroformylation Catalysts

TOYO SODA MANUFACTURING CO. LTD.

U.S. Patent 4,277,414

Catalysts of improved purity are obtained by reducing trans[chlorocarbonyltris(tertiary phosphine) Rh] with Na borohydride in the presence of the tertiary phosphine and in an atmosphere of CO.

Platinum Metal Chalcogenide Hydrosulphurisation Catalysts

EXXON RESEARCH & ENGINEERING CO.

U.S. Patent 4,279,737

S-tolerant catalysts are prepared by low temperature precipitation from non-aqueous solution. Typical catalysts produced by the method are RuS₂, OsS₂, Rh₂S₃ and PdS.

Platinum and Rhodium Catalysts for Release Coatings

IMPERIAL CHEMICAL INDUSTRIES LTD.

U.S. Patent 4,281,093

Pt and Rh organic complexes used to catalyse organopolysiloxane release coatings do not dissolve in the medium and their catalytic effect is diminished if they are used in suspension. Now, in order to avoid the use of toxic solvents, the catalysts are dissolved in low boiling allyl ether solvents.

Platinum Complex Hydrosilylation Catalyst

WACKER-CHEMIE G.m.b.H. *German Offen. 3,000,768*

A catalyst for the hydrosilylation of olefins is obtained by dissolving PtCl_4 in at least 20 times its weight of an olefin, such as octene, and reacting it with a primary or secondary amine, preferably isobutylamine.

Palladium Complex Catalysts

OTDELENIE ORDENA LENINA INSTITUTA

KHIMICHESKOI FIZIKI AN SSSR *Soviet Patent 804,646*

The stereoregular polymerisation of acetylenic monomers is catalysed by Pd complexes with polyvinylpyridine grafted on to polyethylene.

FUEL CELLS

Energy Recovery From Off-Gas

IMPERIAL CHEMICAL INDUSTRIES LTD.

British Patent 1,595,413

In a hydrogenation process energy is recovered by generating electricity by oxidising H_2 in the off-gas in a fuel cell. In one method H_2 in the gas stream is separated by means of a Pd membrane. The process is especially useful for dealing with off-gases from methanation processes which use excess H_2 , especially processes which use Ru, Co and Ni catalysts.

Graphited Felt Flowthrough Electrode for a Fuel Cell

TEXAS INSTRUMENTS INC. *U.S. Patent 4,264,686*

An electrode having greater efficiency and reduced electrical resistance, which may be easily connected to microcircuits, is formed from a graphite-coated felt substrate having a metallic backing plate with one surface coated with a noble metal, preferably Pt.

Solid Polymer Catalytic Electrodes

GENERAL ELECTRIC CO. *U.S. Patent 4,272,353*

Electrodes for use in fuel cells and gas generating cells, which have reduced catalytic loading, are obtained by abrading the surface of a solid polymer electrolyte, with SiC , and then depositing the catalytic metal, (which may be Ir, Pt or another platinum group metal) on to the abraded surface. Heat and pressure may be used to fix the catalyst particles in place.

CHEMICAL TECHNOLOGY

Hard Metal Compacts

SINTERMETALLWERK KREBSOGE G.m.b.H.

British Patent 1,595,517

Metal compacts having controlled hardness and excellent corrosion and heat resistance are prepared from powder mixtures containing a metal powder which may be Fe, Cr, Ni or Co, or where severe working conditions are to be encountered, Pt or Os; up to 25% B, B carbide or Ti boride boronising agent and up to 30% of a boronising activator. In an example borided Pt and diamond composites are used for a bearing which operates in highly corrosive acids.

Growing Crystals

GENERAL ELECTRIC CO.

British Appl. 2,074,891 A

A seed crystal is suspended on a Pt wire in a saturated solution and heated by an i.r. beam so that the crystal grows but no wall deposits are made.

Stabilising Photographic Dye Images

FUJI PHOTO FILM CO. LTD.

U.S. Patent 4,269,926

Pt, Pd, Cu, Ni and Co chelate complexes containing pyridyl benzenethiol and benzothiazine groups are used to prevent u.v. degradation of organic dyes used in photographic materials.

Sensitised Silver Halide Photographic Emulsions

EASTMAN KODAK

U.S. Patent 4,269,927

The speed of high chloride emulsions, especially those sensitised with platinum group metal, Au and other sensitising compounds, is further increased by doping with very low concentrations of divalent metals ions, such as Cd, Pb, Cu or Zn.

Preparation of Metal Powders

JOHNSON MATTHEY & CO. LTD. *U.S. Patent 4,274,877*

Powders having a wide range of potential uses at high temperatures are composites of naturally-occurring refractory materials, such as clays (10–25%), and a finely-divided metal chosen from platinum group metals, Ag, Au and their alloys.

GLASS TECHNOLOGY

Glass Fibre Spinning

OWENS-CORNING FIBERGLAS CORP.

U.S. Patent 4,274,852

Bushings of improved durability for use in glass fibre manufacture are fabricated from a dispersion-strengthened noble metal, preferably Pt or a Pt-Rh alloy strengthened with Zr oxide.

Photochromic Glass

CORNING GLASS WORKS

German Offen. 3,036,103

A clear-to-brown photochromic glass contains AgCl , bromide or iodide and 1–10 ppm of Pd and/or Au.

ELECTRICAL AND ELECTRONIC ENGINEERING

Electroluminescent Diode

THOMPSON-CSF

British Patent 1,600,476

In a method for forming a laser diode, metallic layers which give low resistivity and high resistivity, respectively, are formed on a light emitting substrate. The high resistivity metal is preferably Au separated from the low resistivity layer by a barrier layer of Pt or Pd.

Composite Substrate for Rotating X-Ray Anode Tube

GENERAL ELECTRIC CO. *British Patents 1,602,623/4*

The W or Mo target area is joined to a graphite carrier section via a thin layer of a non-carbide forming metal which is preferably Pt containing up to 1% Cr. Other platinum group metals may be used for the joining layer.

Thermo-Optical Recording System

THOMPSON-CSF *European Appls. 33,430/31, 33,667*

A thermo-optical information-recording system consists of a supported layer of plastic material coated with a metal film. The metal may be Ag-Pt or Cu-Pd or Ni-Pd alloy. In EP 33,667 other suitable alloys are Fe-Pt or Au-Cd alloys.

Electron Tube Cathode

HITACHI LTD.

U.S. Patent 4,260,665

An electron tube cathode of improved durability consists of an annealed Ni-W-Zr alloy substrate containing 20–28% W, coated with a 1,000–2,000 Å film of Pt and then with an electron-emitting layer of a Group IIA metal oxide.

Semiconducting Glasses

CALIFORNIA INSTITUTE OF TECHNOLOGY

U.S. Patent 4,264,358

A series of amorphous glassy alloys containing up to 10 vol.% of flux-pinning crystalline inclusions has potential use in high field superconducting magnets. A preferred alloy is of formula $(\text{Mo}_{06}\text{Ru}_{04}\text{Si}_{10}\text{B}_{10})$.

Hydrogen Storage Materials

SIEMENS A.G.

U.S. Patent 4,265,720

An economical storage material for H_2 consists of amorphous or finely crystalline Si supported on a steel, or quartz glass substrate, and absorbs H_2 under positive pressure, the H_2 being released upon heating to above 50°C. Accelerated H_2 absorption can be obtained if the Si is coated with a thin layer of Pd.

Self-Supporting Resistor Compositions

C.T.S. CORP.

U.S. Patent 4,267,074

The resistors for use in microminiature circuitry are formed by firing a composition containing 0.2% of Ir and/or Ru as a complex which thermally decomposes to the metal oxide, 30–70% of refractory oxide filler (such as Al_2O_3 or SiO_2) and a glass binder.

Tandem Junction Amorphous Silicon Solar Cells

R.C.A. CORP.

U.S. Patent 4,272,641

The active body of a solar cell has two or more layers of hydrogenated amorphous Si arranged in a tandem stacked configuration with one optical path and electrically interconnected by a tunnel junction made, for example, from a PtSiO_2 , PtY_2O_3 , IrSiO or IrY_2O_3 cermet.

Surface Coated Gallium Arsenide Semiconductor Devices

BELL TELEPHONE LABORATORIES INC.

U.S. Patent 4,273,594

The surface recombination velocity of GaAs devices is reduced by coating the surface with a layer of one monolayer or less thickness, of Rh, Ir, Ni, Pb or more preferably Ru.

TEMPERATURE MEASUREMENT

Temperature Measuring Resistors

W. C. HERAEUS G.M.B.H.

British Patent 1,597,403

Thin-film Pt resistance thermometers are more easily manufactured by applying a thin film of Pd, Fe group metal, Cu, Ag or Au to a substrate, masking the thin film and etching away unwanted metal, washing away the mask, coating the whole substrate with a Pt film, alloying it at 400–700°C and finally etching away the alloyed Pt.

MEDICAL USES

Platinum-Clad Bone Joint Prosthesis

JOHNSON MATTHEY & CO. LTD.

British Patent 1,602,375

The corrosion-resistance of stainless steel or Ti prosthetic joints may be improved by coating the moving areas with a pore-free Pt, Ru or Ir alloy. The metals may be alloyed with other precious metals, such as Pd, Rh or Au or with suitable base metals.

Dental Gold-Free Alloys

DEGUSSA A.G.

European Appl. 36,556

Au-free alloys for firing on to ceramics, which do not have the toxicity of Ni dental alloys, contain 1–70% Pd, 0.1–35% Cr, remainder Co, with optional amounts of 0–1% B, 0–20% Mo, and/or W, 0–8% lanthanide and 0–5% Cr, Si, Sn, In and/or Ga. A typical alloy contains 25–35% Pd, 5–15% Cr, 5–15% Mo, 2–6% Ce and 0.2–0.8% B.

Mixed Amine Complexes of Platinum

JOHNSON MATTHEY & CO. LTD. *French Appl. 2,463,776*

New agents for cancer treatment are Pt(II) or (IV) halide complexes of one molecule NH_3 and one molecule of an aliphatic amine, such as a PtCl_2 complex of NH_3 and cyclopentylamine or ethylamine.