

Homogeneous Catalysis of the Water Gas Shift Reaction by Mixed-Metal(Iron/Ruthenium) Catalysts

P. C. FORD, R. G. RINKER, C. UNGERMANN, R. M. LAINE, V. LANDIS and S. A. MOYA, *J. Am. Chem. Soc.*, 1978, **100**, (14), 4595-4597

Ru catalysts for the water gas shift reaction were studied. Ru carbonyl was found to form active catalysts in many reaction media and a mixed Ru and Fe carbonyl catalyst of $\text{Ru}(\text{CO})_{12}$ and $\text{Fe}(\text{CO})_5$ was more active in basic solutions than metal carbonyl. The water gas shift reaction is an important way of making dihydrogen from water, since it derives a larger energy fraction from coal reserves.

An Arene Hydrido-Complex of Ruthenium(II) as Catalyst for the Homogeneous Hydrogenation of Benzene and Olefins

M. A. BENNETT, T.-N. HUANG, A. K. SMITH and T. W. TURNER, *J. Chem. Soc., Chem. Commun.*, 1978, (14), 582-583

Under mild conditions, the complex $[\text{RuHCl}(\eta\text{-C}_6\text{Me}_6)(\text{PPh}_3)]$ is an active homogeneous catalyst for the hydrogenation of benzene giving cyclohexane, and for the hydrogenation of olefins using either molecular hydrogen or secondary alcohols. The catalyst is stable, long-lived and can be easily prepared.

Homogeneous Hydrogenation Catalysed by Tris(diphenyl-p-tolylphosphine)dichlororuthenium(II)

S. VANCHEESAN, S. PRABHA SETHI, J. RAJARAM and J. C. KURIAKOSE, *Indian J. Chem.*, 1978, **16A**, (5), 399-402

Tris(diphenyl-p-tolylphosphine)dichlororuthenium(II) was found to be an efficient catalyst for the homogeneous hydrogenation of selected olefins, such as heptene-1 and 4-methylpentene-1. The rate of hydrogenation increased in the

presence of a basic co-solvent like ethanol but the excess of (diphenyl-p-tolylphosphine) slowed down the rate. The catalyst was found to selectively hydrogenate terminal olefins. However, the hydrogenation slowed down or even stopped in the presence of internal and cyclic olefins.

CHEMICAL TECHNOLOGY

Catalytic Decomposition of Finish Residues

Res. Discl., 1978, (171), 19

During texturing and drawtexturing of continuous filament man-made fibres, deposits form on the heaters and must be removed. A Pt co-ordination complex, such as diamine dinitro Pt(II) is reacted with a neutral mono or bidentate ligand, such as NH_3 ethylenediamine, to form a soluble Pt complex such as tetraamine dinitro Pt(II) or diamine ethylene diamine dinitro Pt(II). This salt is then reacted with hydrazine hydrate on the heater surface to form Pt metal which catalyses the oxidative degradation of the finish residues. Pd may also be used.

Reactions of the Platinum Group Metals at High Temperatures

C. J. RAUB, *Metall.*, 1978, **32**, (8), 802-804

Various uses of platinum group metals for laser technology, the glass industry, catalysis and high temperature electrical technologies are discussed. For high temperature use all need stable form, no reaction between the working material and surrounding atmosphere, good physical reproducibility and constant chemical and physical properties over a wide operational range. The behaviour of platinum group metals, alloys and compounds at high temperatures are examined from these points of view. Their reaction with air, oxygen, other gases, corrosion with liquid metals, alloy formation and optimum properties are discussed.

NEW PATENTS

METALS AND ALLOYS

P.G.M.-Containing Ni and/or Co-Based Alloys

JOHNSON MATTHEY & CO. LTD.

British Patent 1,520,630

The high temperature strength, creep resistance and oxidation and sulphidation resistance of superalloys is increased by incorporation of a platinum group metal. The alloys contain, in wt.%, Ni and/or Co 40-78, Cr trace-23.5, Al and/or Ti trace-7, and trace-6, respectively, and platinum group metal(s) trace-15. Certain other metals and nonmetals may be present in minor proportions.

Noble Metal Ordered Alloys

SONY CORP.

U.S. Patent 4,093,453

Ordered alloys, which can contain Pt, Pd, Au, Ag, Ir and Rh, are produced by providing a solid imperforate metal base of one metal, depositing on it a thin layer of another metal not greater than 10 μm thick, the second metal can form an ordered alloy with the first and heating them.

Ferromagnetic Palladium Alloys

INTERNATIONAL BUSINESS MACHINES CORP.

U.S. Patent 4,098,605

The alloys, for use in magnetic devices and having improved corrosion resistance, contain 20-65 at.% Pd, up to 80 at.% Fe and 0-55 at.% Ni.

Platinum or Gold Foams

U.S. DEPARTMENT OF ENERGY

U.S. Patent 4,099,961

Foamed metals and alloys, including Pt and Au, with a closed cellular structure, are prepared by heating a metal body containing entrapped inert gas to above its melting point and leaving it at this temperature for enough time to allow the gas to expand forming individual cells.

Jewellery Alloy

JOHNSON MATTHEY & CO. LTD.

German Offen. 2,807,587

The alloy contains not less than 95% Pt and 1.5-3.5% Ga together with one or more of Pd, Ru, Ir, Rh, In, Au, Ag, Cu, Co, or Ni and optionally up to 0.1% Y as a deoxidising agent.

Hydrogen-Permeable Alloy

V. A. GOL'TSOV ET AL. *Russian Patent 459,981*

High purity H₂ can be obtained by diffusion through a foil of 10-26% Ag, 1-26% Au, 0.1-2% Al, 0.1-2.5% Pt, 0.1-0.9% Ru and the remainder palladium.

CHEMICAL COMPOUNDS

Osmium Tetroxide Complexes

JOHNSON MATTHEY & CO. LTD.

U.S. Patent 4,100,158

Complexes suitable for fixing and staining cells for biological examination are obtained from OsO₄ and heterocyclic N compounds, such as pyridazine, phthalazine or isoquinoline.

ELECTROCHEMISTRY

Electrolytic Cell

IMPERIAL CHEMICAL INDUSTRIES LTD.

British Patent 1,522,622

An improved design of diaphragm cell for brine electrolysis is described. The cell anodes are preferably of Ti or a Ti alloy with an electrocatalytic coating, such as a platinum group metal or alloy or oxide thereof.

Fuel Cell Electrodes

UNITED TECHNOLOGIES CORP.

British Patent 1,524,379

A method of making a precisely structured gas diffusion electrode is described, fabricated from a mixture of p.t.f.e. particles and Pt supported on C black.

Noble Metal Electrodes

ORBISPHERE CORP. SUCCURSALE DE COLLORIGEBELLEVIVE

U.S. Patent 4,096,047

Electroanalytic transducers for the electrochemical analysis of chemical substances have electrodes formed from noble metals such as Pt, Pd, Ir or Au.

Yttrium Oxide Electrodes

DIAMOND SHAMROCK TECHNOLOGIES

U.S. Patent 4,098,669

Sintered electrodes consist of a self-sustaining matrix of sintered powders of Y oxide and at least one electroconductive agent, with a coating of electrocatalyst(s), such as Rh, Ir, Ru and/or Ag.

ELECTRODEPOSITION AND SURFACE COATINGS

Ruthenium Electrodeposition

INCO EUROPE LTD.

British Patent 1,520,140

Baths stable at all levels of pH, and unaffected by CO₂ absorption, contain Ru in the form of a cationic complex [Ru₂N(NH₃)_xX₂]X₃, where X is Cl, Br or I.

Bright Palladium Plating

SIEMENS A.G.

German Offen. 2,657,925

For reasons of economy, Au is preferably replaced by Pd or a Pd alloy in deposited electrical contacts. Bright, ductile, non-porous Pd layers are obtained from baths which contain no NH₃, the Pd, 1-50 g/l, being present as aminoacetate, and the pH maintained at 7-12 with aminoacetic acid.

LABORATORY APPARATUS AND TECHNIQUE

Gas Sensor

LUCAS ELECTRICAL LTD. *British Patent 1,518,943*

A device for sensing the composition of I.C.E. exhaust gases is a ceramic tile printed with a sensing element consisting preferably of a sintered mixture of TiO₂ with 1 mol % Ta oxide and 1 at. % Pt. Electrical contacts are provided by printing with a Pt and/or Au glass frit composition.

Platinum Crucible for Production of Beryl Crystals

KYOTO CHEMICAL CO. LTD. *U.S. Patent 4,093,502*

In a process for synthesising single crystalline beryl from a molten salt, a Pt crucible, Pt:Pt-Rh thermocouple and Pt wire suspending means are used.

HETEROGENEOUS CATALYSIS

Ergot Alkaloids

SANDOZ LTD.

British Patent 1,519,505

Functional derivatives of lysergic acid are obtained by hydrogenation, such as dihydroergosine from ergosine, over a catalyst such as Pd/C or PdCl₂. In the synthesis a protective group may be present and this is removed by hydrogenolysis over a platinum group metal catalyst.

Amines

AB HASSLE

British Patent 1,524,036

Procedures for synthesising alkylarylamines useful in the treatment of cardiovascular diseases may include the partial or complete hydrogenation of double or triple C-C bonds, which may be catalysed by Pd or Pt, optionally partially deactivated.

Deodorising Device

U.O.P. INC.

British Patent 1,527,516

A device for the catalytic destructive oxidation of malodorous gases, such as cooking fumes, is an electric light bulb coated with an external layer of active material such as Pt, Pd or Ag.

Platinum Group Metal Additives for a Hydrocarbon Cracking Process

MOBIL OIL CORP.

U.S. Patent 4,088,568

A non-hydrogenative endothermic catalytic cracking process for hydrocarbons, especially petroleum fractions, at low pressures and high temperatures, is described in which the endothermic heat required for cracking is supplied by the catalyst as the heat transfer medium. The catalyst is heated by burning the coke deposited on it during cracking, and a decomposable compound of Pt, Pd, Ru, Ir, Os, Rh or Re is introduced into contact with the cracking catalyst during the process. The cracking catalysts used are aluminosilicate zeolites.

Palladium Catalyst for Preparation of Optically Active Amides

HOFFMANN-LA ROCHE INC. *U.S. Patent 4,088,662*

A Pd/C catalyst is used in the production of optically active amides which are intermediates for vitamin E synthesis. The catalyst selectively reduces triple bonds to a double bond.

Cobalt-Ruthenium Catalyst

GULF RESEARCH & DEVELOPMENT CO.

U.S. Patent 4,088,671

Higher hydrocarbons are synthesised from the reaction of CO and H₂ at low pressure in the presence of a catalyst consisting of 1-50% Co, and Ru, the molar ratio Co:Ru being from 5:1 to 100:1.

Platinum Group Metal Hydrogenation Catalyst

EXXON RESEARCH & ENGINEERING CO.

U.S. Patent 4,089,775

A new catalyst is used in a process for simultaneously desulphurising and dewaxing raw, untreated, high S-containing wide-cut petroleum oil fractions to give middle distillate oils of low pour point with a minimum cracking of the raw fraction to gases. It consists of a mixture of faujasite and amorphous silica/alumina support and, as the hydrogenating component, a Group VIb or Group VIII metal oxide and/or sulphide, such as those of Pd, Rh, and Pt.

Ruthenium-Containing Perovskite

JOHNSON MATTHEY & CO. LTD.

U.S. Patent 4,089,810

A catalyst for the purification of I.C.E. exhaust gases consists of an inert porous ceramic honeycomb with a first coating of a high surface area, catalytically active refractory metal oxide and a second layer of a catalytic mixed oxide containing Ru, of formula A₂B₂O₇, ABO₃, B₂O₃ or AB₂O₄ where A is one or more of Na, K, Ca, Sr, Ba, Ag, Cd, Hg, Pb, Bi, Y or lanthanides and B is Ru(IV), and at least one other platinum group metal or Li, Mg, Cr, Nb, As, Au, Ga, In, Sc, Re, Ta, Fe, or Co cation.

Platinum Catalyst for Upgrading Lubricating Oil Stock

MOBIL OIL CORP.

U.S. Patent 4,090,953

Stabilised lubricating oils resistant to oxidation and sludge formation on exposure to oxidative environments, are prepared by upgrading lubricating oil stock by contact with elemental S in the presence of a catalyst which can be Pt.

I.C.E. Catalytic Device

RICARDO & CO. ENGINEERS (1927) LTD.

U.S. Patent 4,092,967

The engine is of the reciprocating-piston type and has a catalytic device for initiating the combustion of the air/fuel charge in the combustion chamber of each cylinder. The fuel has to pass through the catalytic element which is of mesh or grid type and can be made of Pt or Pt coated wire.

Palladium Catalyst

EXXON RESEARCH & ENGINEERING CO.

U.S. Patent 4,093,643

Low molecular weight organic compounds are prepared by passing a mixture of CO and H₂ over a Pd catalyst supported on a suitable acidic metal oxide. The Pd is highly dispersed on the support and has a crystallite size, especially below 40Å. In this state the surface Pd atoms have a much higher activity than the surface Pd atoms of very large crystallites.

Platinum Group and Lanthanide Metal-Containing Zeolites

EXXON RESEARCH & ENGINEERING CO.

U.S. Patent 4,097,410

A cracking catalyst for promoting the oxidation of CO to CO₂ during regeneration of the catalyst by burning the coke from it consists of particles of crystalline aluminosilicate zeolite containing lanthanides and particles of an ultra-stable Y zeolite containing a CO oxidation promoter, dispersed in a porous matrix to produce a catalyst containing 0.8-4.5% lanthanide metal (as oxides) and 2-100 ppm co-oxidation promoter which is a Group VIII metal, Re, Cr and/or Mn, especially Pt, Pd, Rh, Re and/or Ir.

Platinum Group Metal Polymeric Complexes

MOBIL OIL CORP. *U.S. Patent 4,098,727*

The compositions consist of a porous solid styrene/divinyl benzene copolymer, a substituent chosen from amine, thiol, phosphine and arsine, and a Group VIII metal, specifically Rh, Ru or Co, bonded to the substituent. The composition is insoluble in a mixture of olefins, and their corresponding alcohols and aldehydes.

I.C.E. Exhaust Gas Purification

DEUTSCHE GOLD- & SILBER-SCHNEIDANSTALT
German Offen. 2,658,892

A catalytic converter for an I.C.E. exhaust system is a tube of suitable metal with a defined elongated internal gas-flow path, internally coated with ceramic oxide(s), such as alumina, lanthanide metal oxides, and platinum group metal(s), such as Pt and Rh.

Gas Purification

BAYER A.G. *German Offen. 2,703,984*

The purification of gas streams by destructive oxidation of Cl-containing organic compounds is carried out by passing the gas mixture over two successive catalyst beds of supported Pt and supported Pd.

Supported Intermetallic Catalysts

JOHNSON MATTHEY & CO. LTD.
German Offen. 2,804,660

Oxidation and reduction reactions such as the manufacture of HNO₃ and purification of I.C.E. exhaust gases are catalysed by the combination heat-resistant substrate, such as steel or ceramic, refractory oxide coating, where the oxide may be a lanthanide metal oxide and a layer of intermetallic compounds M_xM'_y, where M is Ru, Th, Pd, Ir or Pt and M' may be a lanthanide metal.

Intermetallic Catalysts for Ammonia Oxidation

JOHNSON MATTHEY & CO. LTD.
Dutch Appl. 77.13507

Catalysts for oxidation of NH₃ and other gas phase oxidation and reduction reactions comprise intermetallic compounds of platinum group metals with one or more base metals. Brittleness may be overcome by coating the compounds on a metallic substrate, but certain of the compounds, particularly Ta-Rh, Ta-Ir, Nb-Rh and Nb-Ir are ductile.

Supported Intermetallic Catalyst

JOHNSON MATTHEY & CO. LTD.
Dutch Appl. 78.01298

A wide range of reactions such as NH₃ oxidation and hydrocarbon reforming are catalysed by an intermetallic compound of a platinum group metal and a number of base metals such as AlPt₃, HfIr₃ and TiRu.

Ammonia Decomposition Catalyst

INSTITUT ORGANICHESKOGO KATALIZA I ELEKTRO-KHIMII AN KAZAKHSKOI S.S.R.

Russian Patent 594,994

The decomposition of NH₃ is catalysed by a mixture of Ru (2.7-9%) and Y (0.3-1%) on an Al₂O₃ support.

CHEMICAL TECHNOLOGY

Hydrogen Generation

NATIONAL RESEARCH DEVELOPMENT CORP.
British Patent 1,518,932

H₂ is obtained from water by passing a stream of CO through an aqueous suspension of colloidal transition metal particles. The particles are preferably of a platinum group metal or oxide thereof, particularly Pt.

Polymerisation

SHIN-ETSU CHEMICAL CO. LTD.
British Patent 1,521,058

Scale formation during the polymerisation of vinyl chloride is prevented by lining the reaction vessel with an organometallic complex. Suitable metals include Pd, Pt, Au, Ag, lanthanide metals, Rh or Ir.

Polyvinyl Chloride Emulsions

ELECTRICITY COUNCIL *British Patents 1,525,102-3*
P.V.C. emulsions are concentrated by electrophoresis using an anode which is covered with a porous non-conductive element, on which the solids are deposited and from which they can easily be removed. The anode can be made of Pt, platinised Ti or RuO₂.

GLASS TECHNOLOGY

Liquid Metal Connector

JOHNSON MATTHEY & CO. LTD.
British Patent 1,527,980

An improved bushing for drawing molten glass has a lug which dips into a pool of molten metal to provide an electrical contact, thus eliminating thermal stresses. The liquid metal can be a Ga-In-Sn eutectic and the bushing with its lug can be fabricated from Ru, Rh, Pd, In, Pt, Au, Ag or alloys thereof.

ELECTRICAL AND ELECTRONIC ENGINEERING

Resistors

PLESSEY CO. LTD. *British Patent 1,521,618*

A fused power supply circuit includes an electrical resistor, which is a block of insulating material of substantial mass for dispensing heat, screen-printed with a conductive track connected in

series with a fuse. This is capable of withstanding power surges without burning out before the fuse blows. A second screen-printed track of resistive material may be provided as a continuation of the first track. The material of the first track is a Pd-Ag or Pt-Ag cermet, and of the second track is Ru oxide.

Display Electrode

INTERNATIONAL BUSINESS MACHINES CORP.

British Patent 1,522,049

Improved optical contrast is obtained if a display electrode, preferably Al, with a roughened surface is vacuum coated to a depth of up to 1 μ m with an inert metal such as Pt, Rh, Ru or Ag.

Semiconductor Devices

INTERNATIONAL BUSINESS MACHINES CORP.

British Patent 1,522,294

A method of fabricating field effect transistors is described. The devices include a layer of Al and a layer of Si preferably separated, to prevent chemical reaction between them, by a barrier layer of, for instance, Pt silicide or Pd silicide.

Thermal Printing

OKI ELECTRIC INDUSTRY CO. LTD.

British Patent 1,524,347

Improved heaters for thermal printing heads may be thin layers of Pt with leads of the same metal and conductive layers of, for instance, Au or Ag.

Igniter Electrodes

JOHNSON MATTHEY & CO. LTD.

U.S. Patent 4,081,710

An igniter comprises two electrodes separated by a body of insulating or semiconducting material. At least one electrode comprises a host material preferably containing at least 40% by weight of Co or Ni, up to 20% of one or more of Ru, Rh, Pd, Ir and Pt and one or more of Ni or Co, Ti, Al, W, Mo, Hf, Ta, Fe, Mn, V, Nb, Si, B, C, Re, Zr, Th, and rare earth metals or oxides.

Silver Compositions for Conductor Patterns

E. I. DU PONT DE NEMOURS & CO.

U.S. Patent 4,090,009

Ag conductor compositions for forming highly adherent conductive films on ceramic dielectric substrates consist of finely divided inorganic powder dispersed in an inert liquid vehicle. The powder is made up of 75-91% Ag and Pd metal powder, the ratio of Ag : Pd is 2 : 1 to 15 : 1 and 9-25% inorganic binder which contains 2-6 parts Bi-free glass, 2-9 parts Cu oxide, 2-9 parts polynary oxide containing Ru, Pt, Rh, K, Y and lanthanides and 0-6 parts Pb oxide.

Platinum-Containing Photochemical Diodes

ALLIED CHEMICAL CORP. *U.S. Patent 4,094,751*

Photochemical diodes are described which use light to drive both endoergic and exoergic chemi-

cal reactions so that optical energy is converted into chemical energy. A suitable diode system is n-GaP/Pt in 0.2N sulphuric acid.

Noble Metal Additives for Nuclear Fuel

GENERAL ELECTRIC CO. *U.S. Patent 4,097,402*

Rupture of boiling water reactor nuclear fuel cladding resulting from the embrittlement caused by fission product Cd is prevented by adding the stoichiometrically equivalent amount of Pd, Au or Ag to the fuel.

TEMPERATURE MEASUREMENT

Thermostat

LITTON INDUSTRIES INC. *British Patent 1,519,750*

A thermostatic device for a combined thermal/microwave oven is made of or coated with an electrically conductive high-melting material, which is permanently incapable of absorbing substantial quantities of microwave energy, such as Pt, Rh or Au.

MEDICAL USES

Electrode

MEDTRONIC INC.

British Patent 1,520,351

An electromedical electrode for attachment to the skin comprises flexible adhesive tape coated with powdered Au, platinum group metal or Ag.

Pharmaceutical Implant

SCHERING A.G.

British Patent 1,521,505

Long-acting medication is obtained by implanting in the body a mixture of a pharmacologically active compound with a silicone elastomer obtained by vulcanising a polysiloxane in the presence of Pd, Pt, Rh or Ir.

pH Measurement

F. HOFFMANN-LA-ROCHE & CO. A.G.

British Patent 1,527,334

A single-rod instrument for the in vivo measurement of the pH of human blood includes a Ag layer, a chlorinated Ag wire and a Pt bushing.

Body Fluid Probe

GENERAL ELECTRIC COMPANY

British Patent 1,528,183

A probe for the in vivo determination of, for instance, O₂ and CO₂ in body fluids includes Ag-AgCl₂ reference electrodes and at least one active layer of Pd or Ir metal and oxide.

Dental Alloy

W. C. HERAEUS G.M.B.H. *German Offen. 2,700,853*

The alloy contains 20% Au, 18-22% Pd, 10-14% Cu, 0.1-2% In, 0.05-0.5% Ir and/or Ru, not less than 40% Ag and optionally up to 5% Pt.