Ethylene Glycol from Synthesis Gas via Ruthenium Melt Catalysis

J. F. KNIFTON, *J. Am. Chem. Soc.*, 1981, **103**, (13), 3959–3961

A unique, highly active catalyst system for direct synthesis of ethylene glycol from CO and H_2 (synthesis gas) involving melt catalysis where the Ru source, Ru(IV) oxide or Ru(III) acetylacetonate, is dispersed in a molten quaternary phosphonium or ammonium salt is disclosed. Turnover frequencies may surpass 7.8×10^{-3}/s at 220°C.

CHEMICAL TECHNOLOGY

Experience with Titanium Heat Exchanges in Oil Refineries

K. SUZUKI and Y. NAKAMOTO, *Mater. Perform.*, 1981, **20**, (6), 23–26

A review of Ti and Ti alloys in oil refineries is presented. The Pd thin film (thickness <0.2 μm) coating technique for Ti tube surfaces was developed for tubes in overhead condensers to halt corrosion. Very little corrosion occurred and life expectancy is high.

ELECTRICAL AND ELECTRONIC ENGINEERING

Interaction of Evaporated Palladium Thin Films with Gallium Arsenide

A. OUSTRY, M. CAUMONT, A. ESCAUT, A. MARTINEZ and B. TOPRASERTPONG, *Thin Solid Films*, 1981, **79**, (3), 251–256

The development of semiconductor devices based on GaAs substrates are dependent on the control of the GaAs-metal contacts. A number of ohmic contacts were developed using Pd-based alloys. Pd becomes associated with GaAs during annealing to form $PdAs_2$ alloys at low temperature ($T = 300°C$) and PdGa alloys at $T \geqslant 400°C$. The compounds are closely connected with the thickness of the coated layer. The elements concerned had undergone interdiffusion prior to the formation of the alloy.

A Stable Hydrogen-Sensitive Pd Gate Metal-Oxide Semiconductor Capacitor

M. ARMGARTH and C. NYLANDER, *Appl. Phys. Lett.*, 1981, **39**, (1), 91–92

A Pd gate metal-oxide semiconductor device has serious drift problems which can be eliminated by the introduction of a thin Al_2O_3 layer between the metal and the SiO_2. This makes it possible to use Pd metal-oxide semiconductor devices as stable and accurate H_2 sensors.

TEMPERATURE MEASUREMENT

Interpolation Methods for Platinum Resistance Thermometers between 13.81K and 273.15K

R. C. KEMP, W. R. G. KEMP and L. M. BESLEY, *Metrologia*, 1981, **17**, (2), 43–48

The interpolation process used to determine the values of temperature other than the defining fixed points, measured by a Pt resistance thermometer on IPTS-68 is unsatisfactory. This paper summarises previous attempts to overcome the problems, discusses their advantages and disadvantages and proposes improved schemes.

NEW PATENTS

METALS AND ALLOYS

Thorium-Doped Iridium Alloy for Radioisotope Heat Sources

U.S. DEPARTMENT OF ENERGY *U.S. Patent* 4,253,872

The impact resistance of Ir and Ir-W alloys containing 0.2–2%W used to encapsulate radioisotope fuels in both terrestrial and space applications, is enhanced by the addition of 100–500 ppm of Th. The Th addition assists grain-growth resistance during long term exposure to high temperatures.

Y-Containing Platinum Group Metal-Doped Superalloys

JOHNSON MATTHEY & CO. LTD.

East German Patent 146,305

Superalloys are claimed containing 5–25% Cr, 2–7% Al. 0.5–5% Ti, 0.01–3% Y and/or Sc, 3–15% platinum group metal(s), remainder Ni. These Ni-based alloys are suitable for glass fibre production.

ELECTROCHEMISTRY

Metal-Hydrogen Electric Cells

UNITED KINGDOM ATOMIC ENERGY AUTHORITY

British Patent 1,589,765

In a Ni-H_2 or Ag-H_2 battery a carrier layer between the positive and negative electrodes is vacuum impregnated with an alkaline electrolyte and polyvinyl alcohol to prevent the electrolyte being drawn into the electrode layer by capillary action. Pt-coated negative electrodes are used in the cell.

Method of Raising Steam for Desalination

H. P. A. NELSON *British Appl.* 2,066,293 A

Steam is raised by decomposing distilled H_2O in an electrolyser having Pt, Ag or base metal plated electrodes, recombining H_2 and O_2 in a burner to form superheated steam, which is then converted to a greater tonnage by mixing in a desuperheater with further distilled water.

Iridium Oxide Electrode for Water Electrolysis

R. A. FRASCH & J. R. AYLWARD

U.S. Patent 4,263,112

The electrolysis cell for use with H_2O or water vapour has a highly efficient anode prepared by coating a foraminous support of Ta, Au or Ti with a catalytic mixture containing 65–85% Ir oxide and 15–35% of a high temperature resin binder, such as PTFE.

ELECTRODEPOSITION AND SURFACE COATINGS

Iridium Electroplating

INCO EUROPE LTD. *European Appl.* 29,272

A bath for the electrodeposition of Ir, optionally together with Ru, contains a new complex which is formed by refluxing a diammonium hexahalo-Ir salt with sulphamic acid for about 70 hours.

Chemical Vapour Deposition of Ruthenium

INTERNATIONAL NICKEL CO. INC.

U.S. Patent 4,250,210

Previously proposed methods for vapour depositing Ru have either been slow or involved the use of corrosive Ru compounds. Now Ru can be deposited at relatively high speed using Ru-1,3-diene compounds as a volatile source and a quiescent, low pressure atmosphere. The method is mainly for providing a hard Ru enriched superficial layer on a Co bonded carbide cutting tool.

Brine Electrolysis Electrode

V. L. KUBASOV ET AL. *U.S. Patent* 4,256,563

A new catalytic coating for a valve metal electrode consists of 5–45% platinum group metal oxide, 19–94.9% of at least one Fe group or Mn group oxide and 0.1–50% B oxide. In one example a mixture of 5% RuO_2, 84.3% Mn oxide, 10.3% Co oxide and 0.4% B oxide is used.

Palladium Electroplating

W. C. HERAEUS G.m.b.H. *German Offen.* 2,939,920

Adherent, non-porous Pd deposits are obtained from solutions containing a Pd salt and an amine, such as tetramethyldiamino-propane.

Plating of Refractories

JOHNSON MATTHEY & CO. LTD.

German Offen. 3,035,254

Objects having good stability at elevated temperatures or in oxidising atmospheres, such as resistance thermometers or parts for use in glassmaking, are obtained by coating a non-conductive refractory substrate, such as Mo coated with Al_2O_3, with a sensitising layer, preferably of Pt, chemically or by flame spraying, and then with one or more other platinum group metals by electrolysis from an electrolyte solution or melt.

LABORATORY APPARATUS AND TECHNIQUE

Measurement of the Increase of Bacteria in a Liquid Nutrient

K.K. KYOTO DAIICHI KAGAKU

British Appl. 2,063,911 A

Bacteria increase is measured by detecting a change in the oxidation-reduction potential as measured between a C electrode and a Pt, Ti or W electrode.

Electrochemical Method for Measuring the Constituents of a Gas Mixture

DRAGERWERK A.G. *British Appl.* 2,065,309 A

A cell has a gas diffusion electrode consisting of a Ag plate coated with Pt impregnated polypropylene. A predetermined voltage having an alternating component is applied to the active electrode and the resulting d.c. current obtained is used to determine one constituent of the gas mixture.

Flammable Gas Sensor

INTERNATIONAL GAS DETECTORS LTD.

British Appl. 2,066,963 A

The sensitivity of a catalytic gas detector is considerably increased if the Pt, helically wound, filament is encapsulated in a porous gas diffusive skeletal matrix formed by interspersing Al_2O_3 particles between particles of Pt or Pd catalyst material. The sensor has increased resistance to atmospheric poisoning by trace Si and S compounds.

Fluid Flow Sensor

HITACHI LTD. *British Appl.* 2,068,173 A

A relatively cheap sensor is prepared by coating a tube with a Pt layer by firing a Pt paste and then laser cutting a spiral track in the film.

HETEROGENEOUS CATALYSIS

Rhodium-Loaded Mordenite Hydrocracking Catalyst

NORTON CO. *British Patent* 1,589,661

A H_2 mordenite having a specified SiO_2:Al_2O_3 mole ratio, loaded with at least 0.2% of elemental Rh, is effective for hydrocracking hydrocarbons to gasoline range products. The catalyst may also contain Pd in combination with the Rh.

Intermetallic Catalysts

JOHNSON MATTHEY & CO. LTD.

British Patent 1,590,451

Pt metal loss from NH_3 oxidation gauze catalysts and from other catalysts used in oxidising and reducing reactions is reduced if the catalyst is in the form of an intermetallic A_xB_y where A is Ru, Rh, Pd, Ir or Pt and B is Al, Sc, Y, the lanthanides, Ti, Zr, Hf, V, Nb or Ta deposited onto a refractory metal oxide, itself carried on a metallic substrate.

Production of Hydrocarbons by Hydrocracking Coal

L. RAICHLE & W. KROENIG *British Patent* 1,590,963

A Pt-Re hydrogenation catalyst may be used in a process for producing hydrocarbon oils from coal which uses an asphatene-free oil mixture for slurrying the coal.

Hydrocarbon Hydroalkylation Process

PHILLIPS PETROLEUM CO. *British Patent* 1,592,375

A highly active and selective catalyst, which can be regenerated by air burn-off, consists of Pt deposited on a type X or Y zeolite which has been ion exchanged with ammonium, Ni and at least one lanthanide, such as a commercial lanthanide mixture.

Explosion Proof Bed for Catalytic Heaters

A. C. KIRKBY *British Patent* 1,592,440

Pt and Pd have been impregnated onto amphibole asbestos material to form explosion-proof catalytic heaters and since the special asbestos is no longer available, alternative materials, have been sought. Now by adding Fe oxide to either the bed or the catalyst materials, normally explosive materials, such as Al_2O_3, may be used for the catalyst bed.

Manufacture of Olefins and Aromatics from Coal Derived Oils

COAL INDUSTRY (PATENTS) LTD. *British Appl.* 2,062,668 A

A coal derived oil fraction is hydrogenated over a platinum group metal or base metal catalyst and then, after stripping the hydrogenated oil of light ends, the product is cracked to yield an olefin and mononuclear aromatic containing product.

Fibre Packs for Ammonia Oxidation

JOHNSON MATTHEY & CO. LTD. *British Appl.* 2,064,975 A

Catalyst pads useful in HNO_3 acid plants are formed from an agglomeration of platinum group metal, Au or Ag (or alloy) fibres which have been welded or sintered together. The fibre pads are preferably held between two conventional Pt-Rh or Pt gauze pads.

Ozone Removal Catalysts

U.O.P. INC. *British Appl.* 2,067,912 A

A filter containing Pt and Rh or other platinum group metals and a carbonaceous pyropolymer composited on an Al_2O_3 support decomposes O_3 present in the atmosphere without the release of particulate matter.

Selective Hydrogenation Catalyst

IMPERIAL CHEMICAL INDUSTRIES LTD. *European Appl.* 29,321

A catalyst for the selective hydrogenation of highly unsaturated hydrocarbons in the presence of less unsaturated hydrocarbons consists of a calcined, shaped calcium aluminate carrier impregnated to a depth of not more than 300 μm with Pd.

Reforming Catalyst

EXXON RESEARCH & ENGINEERING CO. *European Appl.* 31,700

A hydrocarbon-reforming catalyst for use in a magnetically stabilised fluidised bed is preferably obtained by combining an Al_2O_3 powder impregnated with Pt with a non-impregnated Al_2O_3 powder and a stainless steel powder.

Catalysts

BRITISH PETROLEUM CO. LTD. *European Appl.* 33,212

Ethanol, acetaldehyde and/or acetic acid are obtained by reaction of CO with H_2 in a liquid medium in the presence of a catalyst which is Rh, optionally supported on SiO_2 and preferably promoted with other metal(s) such as Ru and Ag. The reaction medium may also contain as co-catalyst a soluble compound of a platinum group metal.

Acidic Multimetallic Catalyst

U.O.P. INC. *U.S. Patent* 4,250,055

A catalyst, for hydrocarbon conversion contains 0.01–2% of a platinum group metal, 0.1–10% U, 0.05–5% Ni and up to 3.5% of a halogen component.

Ammonia Synthesis Catalyst

BRITISH PETROLEUM CO. LTD. *U.S. Patent* 4,250,057

Highly active NH_3 synthesis catalysts consist of 0.1–50% of a transition metal, preferably Ru, Co and/or Rh and a modifying amount of a Group IA, IIA, lanthanide and/or actinide metal supported on a high basal surface area C containing graphite.

Platinum-Palladium-Rhenium Reforming Catalysts

EXXON RESEARCH & ENGINEERING CO. *U.S. Patent* 4,251,392

A catalyst containing 0.2–0.6% Pt and Pd, 15–50 mol.% being Pt, 0.1–2% Re, 0.1–0.1% Cu and a halogen component, has reduced hydrogenolysis reaction when used in naphtha upgrading reactions.

Fluid Catalytic Cracking Process

MOBIL OIL CORP. *U.S. Patent* 4,251,395

Up to 10 ppm of Pt are added to the cracking catalyst used in a fluid catalytic cracking process as a dehydrogenation component to reduce the CO content of flue gases emanating from the catalyst regeneration zone.

Triple Layer Oxygen and Hydrogen Recombination Catalysts

HITACHI LTD. *U.S. Patent* 4,252,690

A metallic support is provided with an intermediate layer having high heat insulating or surface area increasing properties, before application of the catalyst layer. In the examples, an Al_2O_3 intermediate layer is used with a Pd catalyst for removing O_2 and H_2 from nuclear reactor off-gases and Ti is used as an intermediate layer in a Pt catalyst for removing acetylene from exhaust gases.

Underwater Power Systems

JOHNSON MATTHEY & CO. LTD. *U.S. Patent* 4,254,739

Power sources for use underwater include two or more catalytic burners, each consisting of a fuel injector and a specified supported platinum group metal catalyst. Each burner is provided with a separate fuel supply and heat exchanger and the burners are connected in series.

Combustion

JOHNSON MATTHEY & CO. LTD. *U.S. Patent* 4,257,223

In a system of improved efficiency, the exhaust gases from a gas turbine, with some additional fuel, are passed through a monolithic catalytic burner which may be made of (or coated with) Au, Ag, platinum group and/or lanthanide metal.

Platinum-Iridium Reforming Catalyst

MOBIL OIL CORP. *U.S. Patent* 4,263,134

The activity, selectivity and resistance to S poisoning of a Pt-Ir naphtha reforming catalyst is improved if each metal is deposited separately on to individual Al_2O_3 support particles. The Pt component may contain other catalytic metal promoters, such as Ag, Os, Cu, Au, Pd, Rh, Ga, Re, Ge and /or Sn.

Foldable Gauze Pack

JOHNSON MATTHEY & CO. LTD. *French Appl.* 2,455,557

Getter sheets, for use with Pt-Rh catalyst gauzes, which are rigid enough to allow easy installation and removal from the reactor, are formed from a substrate such as of, stainless steel carrying a segmented getter layer of a Pd-Au alloy material, for example. The segments may be sectors of a circle or in the form of a quadrant.

Platinum-Tin Catalyst for Hydrocarbon Hydrotreatment

CIE. FRANCAISE DE RAFFINAGE *French Appl.* 2,457,318

An effective catalyst for upgrading hydrocarbon to high octane ratings consists of a refractory oxide support, 0.2–2% of a platinum group metal, preferably Pt, 0.02–2% of Sn and, in combined form, a specified ratio of a Group IA and a Group IIA metal.

Selective Hydrogenation Process

INSTITUT FRANCAIS DU PETROLE *French Appl.* 2,458,524

Unsaturated hydrocarbons containing 2–3C atoms are selectively hydrogenated in a feedstock using a Pd/Al_2O_3 catalyst with 50Å dispersed Pd crystallites.

HOMOGENEOUS CATALYSIS

Hydroformylation Process

UNION CARBIDE CORP. *European Appl.* 31,590

In a Rh-catalysed hydroformylation process for producing aldehydes from olefins, propionaldehyde is also obtained by using ethylene as a co-reactant. The catalyst may be $Rh(CO)(acac)(PPh_3)$.

Ruthenium Catalyst for Alcohol Oxidation

INSTITUT FRANCAIS DU PETROLE *U.S. Patent* 4,250,121

Carbonyl compounds are prepared by oxidising alcohols and polyalcohols in the presence of a Ru complex, such as Ru trifluoroacetate, in association with a Cu or Fe salt or complex such as a Cu perchlorate hexamethylphosphorotriamide complex.

Preparation of Aminomethyl Cyclododecane Corrosion Inhibitors

BAYER A.G. *U.S. Patent* 4,251,462

The inhibitors, for use in oils and motor fuels, are prepared by the hydroformylation of cyclodecatriene in the presence of a Rh catalyst, such as tris(dibenzyl sulphide) $RhCl_3$, and optionally a Co component, and subsequent hydrogenation.

Anionic Group VIII Metal Hydride Catalysts for Nitrile Hydrogenation

ALLIED CHEMICAL CORP. *U.S. Patent* 4,254,059

Anionic Pt, Rh, Ru and Fe hydride catalysts containing P, As or Sb organic ligands are effective homogeneous catalysts for the hydrogenation of nitriles to primary amines.

Rhodium Complex Catalysts

UNION CARBIDE CO. *U.S. Patent* 4,257,972

The formation of polyols from synthesis gas is preferably catalysed by a Rh carbonyl phosphide cluster complex, such as $Cs_2[Rh_9P(CO)_{21}]$.

Palladium Complex Catalysts

E. I. DU PONT DE NEMOURS & CO. *U.S. Patent* 4,257,973

The formation of carboxylic acids or esters from olefins, CO and H_2O or a primary or secondary alcohol is catalysed by a Pd halide phosphine complex.

Carbonylation Catalysts

HOECHST A.G. *German Offen.* 2,939,839

The formation of acetic anhydride from methyl acetate and CO is catalysed by a system containing Rh or Ir chloride or Pd acetate.

Olefin Hydroformylation Catalyst

MITSUBISHI CHEMICAL INDUSTRIES LTD. *German Offen.* 3,035,468

In a specified process for olefin hydroformylation the catalyst is Rh-triarylphosphine complex and an excess of the phosphine is used.

FUEL CELLS

Hydrogen Generation

UNITED TECHNOLOGIES CORP. *European Appl.* 29,628

H_2, for use in fuel cells, is generated by electrolysing an aqueous solution of HBr using an amorphous Si anode and a Pt cathode. The amorphous Si is preferably coated with an extremely thin (50Å) Pt layer.

Solid Electrolyte Electrolytic Cell

UNITED TECHNOLOGIES CORP. *U.S. Patent* 4,248,941

A thin-film fuel cell has spaced-apart or side-by-side catalyst layers as electrodes with the gap between the catalyst layers being bridged by a solid electrolyte. The cathode and anode catalysts used in the cell are preferably Pt but may also be selective O_2 reduction catalysts, such as $SrRuO_3$.

Electric Current Generation from Hydrazine

UNITED TECHNOLOGIES CORP. *U.S. Patent* 4,251,601

Hydrazine is fed to a generator having a porous membrane and electrodes made of different metals. The electrodes are initially energised by dissociating the fuel by contact with an Ir/Al_2O_3 or other fuel decomposition catalyst. One set of fluid electrodes used in the cell may be screens or a granular bed of steel, Fe, Ni, Co, Cu, Ag, etc. and the other of Mg, Y, La or Al.

Highly Stable Fuel Cell Electrodes

INSTITUTE OF GAS TECHNOLOGY *U.S. Patent* 4,263,376

The electrocatalyst of a gas diffusion electrode is supported on material containing nitrogenous groups which react with the electrocatalyst metal. In a preferred method amide groups chemically bonded to a C support for a Pt catalyst provide highly stable diffusion electrodes for phosphoric acid fuel cells.

ELECTRICAL AND ELECTRONIC ENGINEERING

Electron Emitter

E.M.I.-VARIAN LTD. *British Patent* 1,591,789

An emitter material is prepared by subjecting a powder containing a refractory metal (Ir, Os, Pt, Mo, Ni, Re, Ru and/or W), a Ba compound activator and a reducing agent which may be Pr, La, Y, Sm, Nd and Sc, among others, to high energy milling action for sufficient time to reform the powder into grains which are welded together with the metal activator dispersed throughout the open structured matrix.

Heat Resistant Spring

SUMITOMO CHEMICAL CO. LTD. *British Appl.* 2,062,075 A

A heat resistant spring consists of a high melting metal matrix, which may be Pd, Y, La, Ag, Au or a base metal alloy, reinforced with an inorganic fibre, such as Al_2O_3, having a high modulus of elasticity.

Solar Cell

LICENTIA PATENT-VERWALTUNGS G.m.b.H. *British Appl.* 2,062,351 A

Solar cells are provided with Ti-Pd-Ag contact pads on the light receiving surface and then the whole of this surface, including the contacts, is covered with a reflection-reducing layer.

Method of Forming Self Registering Contacts on FET Structures

HEWLETT PACKARD CO. *British Appl.* 2,062,959 A

Source, drain and gate contacts are made via an etchable polysilicon layer. The contact layer is preferably Pt silicide deposited on electrically conductive regions formed on the unexposed polysilicon.

Palladium-Gold Thick Film Conductors

ELECTRO MATERIALS CORP. OF AMERICA *British Appl.* 2,063,570 A

Thermal runaway in an integrated circuit (ic) chip having Pd-doped Au thick film conductors is reduced by increasing the surface area of the Pd. The method also assists eutectic die attachment of Al lead wires to the ic. A typical thick film resistor is formed from a paste containing 87–88% Au, 1.41% Pd, 0.43% Pt, 1.41% ZnO and BiO_2 together with a glass frit.

Garnet-Based Magnetic Bubbles

WESTERN ELECTRIC CO. INC. *British Appl.* 2,066,236 A

The normal lanthanide ions are replaced by Ir, Ru or Co in the octahedral site of the garnet. This gives high mobility and high magnetic anisotropy.

Platinum Complex Coated Recording Medium

R.C.A. CORP *British Appl.* 2,066,490 A

A Pt complex coated medium for laser recording, has a substrate coated with a reflective layer of Rh, Au or Al, and then with a light absorbing layer which contains a Pt complex of bis(dithio-α-ketones).

Energetic Particle Beam Deposition

INTERNATIONAL BUSINESS MACHINES CORP. *U.S. Patent* 4,250,009

An improved sputter deposition and etching process uses an angled target composed of an intermetallic compound where one of the metals is Pt, Ir, Os, Hg, Au, Sb or Zn, and the other is a Group IA, Group IIA or lanthanide metal.

Electrochromic Iridium Oxide Electrodes

BELL TELEPHONE LABORATORIES INC. *U.S. Patent* 4,258,984

Electrodes for electrochromic devices are produced by sputtering directly from an Ir target in an O_2 atmosphere to produce an Ir oxide film.

MEDICAL USES

Platinum Encapsulated Cardiac Pacemakers

NEEDLE INDUSTRIES LTD. *U.S. Patent* 4,248,237

Metallic pacemaker bodies, such as Ti or stainless steel, may fail due to electrolytic corrosion and those made from epoxy resins fail due to moisture swelling and cracking. To overcome these problems the bodies, now made of plastic, are encapsulated in a skin of Pt having a thickness of 0.1875–0.5 mm.