

Hydrogenolysis in Hydrazo-Benzene Interaction with Propan-2-ol in the Presence of Rhodium and Ruthenium Triphenylphosphine Complexes

B. M. SAVCHENKO, V. Z. SHARF, V. N. KRUTII and K. KH. FREIDLIN, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, (11), 2632-2634

Complexes $\text{RhCl}(\text{PPh}_3)_3(\text{I})$ and $\text{RuCl}_2(\text{PPh}_3)_3(\text{II})$ catalyse the H transfer reaction from propan-2-ol to hydrazo-benzene forming aniline. The addition of KOH to the complex solution (I) promotes the hydrogenolysis of N-N bond of hydrazo-benzene. However, the reaction of hydrogenolysis of hydrazo-benzene catalysed only by alkalis is slower than the reactions catalysed by Rh complexes (I) and (II).

A Convenient Synthesis of Cyclopentanones via Rhodium(I)-Catalysed Intramolecular Hydroacylation of Unsaturated Aldehydes

R. C. LAROCK, K. OERTLE and G. F. POTTER, *J. Am. Chem. Soc.*, 1980, **102**, (1), 190-197

The Rh(I) catalysed intramolecular hydroacylation of unsaturated aldehydes was investigated and three new catalyst systems were developed. The catalysts were prepared from chlorobis(cyclooctene)Rh(I) dimer and 2 equivalents of tri-*p*-tolylphosphine, tri-*p*-anisylphosphine or tris(*p*-dimethylamino-phenyl)phosphine in methylene chloride saturated with ethylene. With these, 4-5-unsaturated aldehydes are catalytically cyclised to cyclopentanones. Substitution in the 2 and 5 positions reduces the yield of cyclic ketone and corresponding ethyl ketones appear as side products. This procedure is applicable to the synthesis of spirocyclic and fused bicyclic ketones.

NEW PATENTS

METALS AND ALLOYS

Dispersion Hardened Platinum Metals

COMPTOIR-LYON-ALEMAND-LOUYOT

British Appl. 2,023,667 A

Dispersion hardened Pt, Pt-Rh, Pt-Ir and other platinum group metal alloys are produced by spraying the molten alloy and the refractory oxide additions such as 0.2-1% Y oxide onto a target, at high pressure.

Jewellery Alloys

JOHNSON MATTHEY & CO. LTD. *U.S. Patent* 4,165,983

Jewellery alloys having improved castability compared with known Pt alloys contain at least 95% Pt, 1.5-3% Ga, the balance being In, Au, Pd, Ag, Cu, Co, Ni, Ru, Ir and/or Rh. A Ga-Au-Pt alloy is preferred for ornamental applications and a Ga-In-Pt alloy, optionally including Au, Ag or Pt, for the manufacture of springs and clasps.

Homogeneous Catalysis of the Water Gas Shift Reaction by Ruthenium and Other Metal Carbonyls. Studies in Alkaline Solutions

C. UNGERMANN, V. LANDIS, S. A. MOYA, H. COHEN, H. WALKER, R. G. PEARSON, R. G. RINKER and P. C. FORD, *J. Am. Chem. Soc.*, 1979, **101**, (20), 5922-5929

Homogeneous catalysis of the water gas shift reaction $\text{H}_2\text{O} + \text{CO} \rightleftharpoons \text{H}_2 + \text{CO}_2$, has been demonstrated for a number of metal carbonyl complexes under alkaline conditions. For Ru carbonyl in aqueous ethoxyethanol solution the principal species present were $\text{H}_3\text{Ru}_4(\text{CO})_{12}^-$ and $\text{HRu}_3(\text{CO})_{11}^-$. The catalysis rate is first order in CO partial pressure and the total Ru concentration. Catalysts prepared by adding both Ru and Fe carbonyls to the same solution are more active than either catalyst alone.

ELECTRICAL AND ELECTRONIC ENGINEERING

Ru and RuO₂ as Electrical Contact Materials: Preparation and Environmental Interactions

R. G. VADIMSKY, R. P. FRANKENTHAL and D. E. THOMPSON, *J. Electrochem. Soc.*, 1979, **126**, (11), 2017-2023

Ru and RuO₂ were evaluated as electrical contact materials for use at low voltages. The contact resistance of RuO₂ was 1mΩ, only slightly higher than that of Ru and Au. Ti coated with RuO₂ has contact resistance of <15mΩ. Ru and RuO₂ are stable at temperatures up to at least 90°C and at all relative humidities, even in the presence of 1 ppm H₂S or flowers of S vapour.

CHEMICAL COMPOUNDS

Rhodium Complexes

CALIFORNIA INSTITUTE OF TECHNOLOGY

U.S. Patent 4,169,030

Deep blue "Rh bridge" complex ions, dirhodium tetrakis(1,3-diisocyanopropane), in water when irradiated between 500 and 600 nm cause direct reduction of the protons in water to H₂, converting the Rh bridge to a yellow form. This H₂ producing visible photo-reaction can be used in a solar-driven water splitting cycle.

ELECTROCHEMISTRY

Electrodes for Membrane Cells

SOLVAY & CIE.

British Patent 1,556,253

Vertical electrodes in gas-producing electrolytic cells, such as water electrolytic cells, have vertical slots with angled vanes along their edges to prevent gas

build-up within the cell. The electrodes are usually formed from Pt metal or Pt metal oxide coated valve metal.

Electrodes

INCO EUROPE LTD.

European Appl. 7,239

Insoluble electrodes specially useful in the electrowinning of Ni consist of a conductive substrate, such as Ti, a barrier layer of platinum group metal(s) and/or Au, an electrodeposited layer of Ru and Ir and an outer layer containing at least 80% RuO₂.

Fuel Cell Electrode

LOCKHEED MISSILES & SPACE CO. INC.

U.S. Patent 4,163,084

Improved results are obtained in the electrochemical reduction of Cl₂, O₂ or peroxy ions in aqueous alkaline media when the cathode is coated with a continuous layer of Ru.

ELECTRODEPOSITION AND SURFACE COATINGS

Platinum-Clad Articles

JOHNSON MATTHEY & CO. LTD.

U.S. Patent 4,163,736

The articles, for use at high temperatures and in non-oxidising or reducing conditions, consist of a refractory core, a sheath of platinum group metal or its alloy and a barrier layer of magnesia between the core and the sheath.

Surface Activator for Electroless Plating

VORONEZHSKII TEKHNOLIGICHESKII INSTITUT

Russian Patent 654,658

Non-conductive surfaces are activated for chemical plating by immersion in a solution containing 100 g epoxy resin, 100–400 g phenolic resin, 1–4 l acetone, 20–50 g PdCl₂, 360–650 g HCl and 6–80 g of a reducing agent which is hydrazine, hydroxylamine or resorcinol.

LABORATORY APPARATUS AND TECHNIQUE

Microflow Sensors for Gases

LEYBOLD-HERAEUS-VERWALTUNG G.m.b.H.

British Patent 1,556,979

Damage caused by vibration and shocks to sensors of the hot wire anemometer type is reduced by using a single connecting lead between both Pt resistance thermometer elements and the central Pt–Ir heating wire. Two other leads are connected to the heating wire via insulating glass beads.

Solid Electrolyte Sensor

GENERAL MOTORS CORP.

British Appls. 2,017,925/6/7 A

The heater and tubular reference electrode of a solid electrolyte oxygen sensor are formed on a sub-

assembly, which ensures electrical isolation and correct alignment of the two components. Fired Pt paste electrodes and Ag contact coatings are used in the sensor.

Self-Humidifying Hydrated Solid Polymer Gas Sensor

GENERAL ELECTRIC CO.

U.S. Patent 4,171,253

Catalytic sensing, reference and counter electrodes, formed from a Pt–Ir–PTFE mixture, are used on a potentiometric sensor which is humidified by flooding one side of its membrane with distilled water.

HETEROGENEOUS CATALYSIS

Platinum Metal Catalyst Alloys

SOLVAY ET CIE.

British Patent 1,555,817

Particulate alloys containing Pd, Ir, Rh, Ru and/or other platinum group metal(s), and Ag, Bi, Cd, Co, Cu, Mo, W and/or Zn are prepared by reducing mixed metal oxides containing the metals. The alloys have a surface area between 0.5 and 800 m²/g and a mean diameter between 10 and 10,000 Å and are used in the preparation of catalysts.

Alternating Reforming and Isomerisation Process

CHEVRON RESEARCH CO.

British Patent 1,556,575

A process for alternately reforming naphtha and isomerising alkyl aromatic compounds uses a single catalyst containing 0.01–3% Pt, at least 0.5% combined halogen and optionally 0.01–3% Re on an Al₂O₃ support.

Destruction of Organic Chlorine Compounds

BAYER A.G.

British Patent 1,556,636

Compounds such as chlorobenzene are converted to CO₂ by passage over two beds of catalysts, the first containing Pt and the second containing Pd/Al₂O₃.

Exhaust Gas Purification Catalyst

FORD MOTOR CO. LTD.

British Patent 1,558,004

A catalyst for treatment of I.C.E. exhausts, of the equilibrium type, consists of 10–5,000 ppm Rh, 500–10,000 ppm Pt or Pd, 500–50,000 ppm of an O₂ storage metal preferably Re, and 50–10,000 ppm of Ru or W on a refractory oxide treated substrate. The catalyst can cope with engine operating conditions which temporarily produce O₂-deficient exhaust gases.

Phenylene Diamines

AKZO N.V.

British Appl. 2,018,775 A

Asymmetrical N-phenyl-N-substituted p-phenylene diamines, used as rubber antioxidants, are obtained by the reaction of p-nitroso-diphenyl hydroxylamines with aldehydes or ketones in the presence of H₂ and a catalyst which is an activated C carrier of surface area not less than 700 m²/g supporting Pd sulphide or Pt sulphide.

Nitroaromatic Compound Hydrogenation

JOHNSON MATTHEY & CO. LTD.

British Appl. 2,022,586 A

When Pd catalysts are used in the hydrogenation of nitroaromatic compounds, the metal tends to dissolve in the reaction medium. This is now avoided by maintaining a H₂ excess round the catalyst.

Hydrocarbon Synthesis

JOHNSON MATTHEY & CO. LTD.

British Appl. 2,024,246 A

Hydrocarbons and especially gasoline are synthesised from H₂ and CO over a supported Ru catalyst using a temperature in the range 500–525 K and a CO pressure of at least 0.8 atm or a temperature in the range 525–550 K and a CO pressure of at least 3 atm.

Platinum Metal/Vanadium Fuel Cell Catalysts

UNITED TECHNOLOGIES CORP.

British Appl. 2,024,869 A

An alloy of a platinum group metal, preferably Pt, and V provides high activity cathode catalysts for fuel cells. The alloy is prepared by reacting V with Na dithionite to form a sol of a finely dispersed V sulphite complex and then reacting platinum group metal particles in a reducing atmosphere.

Decomposition of Organic Chlorine Compounds

RHONE-POULENC INDUSTRIES *European Appl. 5,655*

Effluent gases containing organic chlorine compounds, from vinyl chloride manufacture, are purified by oxidative destruction of the pollutants over a bed of Pt and/or Ir supported on η -Al₂O₃.

Cracking Catalyst

EXXON RESEARCH & ENGINEERING CO.

U.S. Patent 4,164,465

A catalyst which is easily decoked consists of an inorganic porous oxide matrix in which are embedded a Y-type zeolite, preferably ion exchanged with a platinum group metal, and an X-type zeolite.

Catalyst Pad

TORAY INDUSTRIES INC.

U.S. Patent 4,169,911

A porous material composed of cut C fibres, 2–3 μ m in diameter, covered with a thin metal film, which may be a platinum group metal, Au or Ag amongst others, may be used for a wide range of applications; these include battery electrodes, filters and supports.

Lanthanide Metal/Platinum Group Metal Catalysts

W. R. GRACE & CO.

U.S. Patent 4,170,573

Ce, La and Al oxide composite substrates carrying a catalytic amount of a platinum group metal (Pt-Ir) are effective for promoting the combustion of carbonaceous fuels at high temperature (above 1317°C) with low CO and NO_x emission.

Stirling Engine with Catalytic Combustor

JOHNSON MATTHEY & CO. LTD.

German Offen. 2,918,320

Catalytic oxidation of a major proportion of the fuel in a Stirling engine takes place in an external combustor enabling the engine to be used where noise and pollution limits apply. The catalytic metal or alloy such as Pt-Rh, is supported on a monolith coated with an oxide such as Al₂O₃.

HOMOGENEOUS CATALYSIS

Homogeneous Ruthenium Catalysts

TEXACO DEVELOPMENT CORP. *U.S. Patent 4,169,853*

Ru-containing complexes in combination with quaternary ammonium hydroxides effect the catalytic hydrogenation of ortho-substituted mononitro aromatics to corresponding aryl amines. Tris(triphenylphosphine) Ru chloride is used.

Hydroformylation

CELANESE CORP.

U.S. Patent 4,169,861

Ru complexes containing ferrocene bidentate and monodentate ligands are particularly effective for achieving straight chain aldehyde formation from olefins, under mild conditions. A preferred bidentate ligand is bis(diphenyl-phosphino)ferrocene.

Ruthenium/Pyridine and Iridium/Pyridine Catalysts

GULF RESEARCH & DEVELOPMENT CO.

U.S. Patents 4,170,605/6

Ethylene glycol is selectively prepared by contacting CO and H₂ over a Ru tris(acetylacetonate)-pyridine or an Ir dicarbonyl acetylacetonate-pyridine catalyst.

CHEMICAL TECHNOLOGY

Solvent Resistant Silicone Rubber

GENERAL ELECTRIC CO. *British Patents 1,557,987/8*

SiH-olefin Pt-catalysed silicone rubber compositions having fluorinated substituent radicals show improved solvent resistance over known room temperature vulcanisable silicone rubbers.

Flame-Retardant Silicone Compositions

DOW CORNING CORP.

British Patent 1,558,805

Flame-resistant silicone compositions, which are curable with conventional bis(t-butylperoxy) dimethylhexane contain 10–150 ppm of a Pt compound, in addition to known flame-retardants, such as lanthanide metal oxides.

Glossing/Burnishing Lubricant

JOHNSON MATTHEY & CO. LTD.

British Appl. 2,023,644 A

Lubricants for turning and/or burnishing operations on Pt and Pt base metals are based on gelatine and water. A rust inhibitor and/or a fungicide may be added to the lubricant. High surface finishes are obtained with less tool wear.

GLASS TECHNOLOGY

Glass Working Tools

N.V. PHILIPS' GLOEILAMPENFABRIEKEN

British Appl. 2,021,095 A

Glass handling and shaping tools made from porous W or Mo are coated with a boride, B carbide or a B alloy to prevent the glass sticking to the tool. The tool surface is preferably further coated with Pd which allows B diffusion. Alternatively a Pd-5% B alloy may be used as the coating material.

ELECTRICAL AND ELECTRONIC ENGINEERING

Magnetic Particle Separation

UNITED KINGDOM ATOMIC ENERGY AUTHORITY

British Patent 1,555,670

Pt metal-coated ferromagnetic spheres, particularly spheres coated with a 77% Pt-23% Co alloy, are used as collectors in an electromagnetic particle recovery system for solutions emanating from the dissolver of a nuclear fuel reprocessing plant.

Ruthenium Oxide Resistor Compositions

E. I. DU PONT DE NEMOURS & CO.

British Patent 1,556,850

Fired resistor compositions having a low coefficient of variation in resistivity as well as a low TCR are prepared from a composition containing 2-45% of finely divided RuO₂ powder, 40-70% of a Pb oxide glass, 0.1-0.8% Nb₂O₃ and 0-5% of CaF₂ in an inert vehicle.

Ignition Distributor

NISSAN MOTOR CO. LTD.

British Patent 1,558,638

A distributed constant RC circuit used in a distributor for the production of a spark employs an Al₂O₃ or other oxidic baseplate coated with a resistive film. The film may be produced from Ru oxide or a Ag/Pd mixture and a glass frit.

Semiconductor-Liquid Junction Photocell

WESTERN ELECTRIC CO. INC.

British Appl. 2,021,314 A

Addition of Ru to the surface of a n-type GaAs electrode of a solar cell alters electronic states so as to reduce surface recombination and increase the conversion efficiency of the cell. Rh may be used as less efficient alternatives to Ru, which is present in amounts between 0.1 and 5 monolayers.

Temperature Coefficient of Resistance Control in a Resistance Material

N. V. PHILIPS' GLOEILAMPENFABRIEKEN

British Appl. 2,021,554 A

The particles of ceramic material forming resistance films are coated with a compound of a metal which may be converted to an oxide which influences the TCR of the film. The examples show the use of lead borosilicate particles coated with Ru oxide, K

ruthenate particles coated with Cu oxide and Bi ruthenate particles coated with Pb oxide.

Schottky Diode

INTERNATIONAL RECTIFIER CORP.

British Appl. 2,022,318 A

A Schottky junction is formed between a high work function metal, such as Mo, and an intermetallic alloy of Pd or Pt with Si. The alloy is formed at the surface of an epitaxial Si layer by sintering and the Pt is sheathed with Mo before sintering takes place. The Mo surface is covered by Ti, Ni and Ag.

Schottky Barrier Layer Contact

INTERNATIONAL BUSINESS MACHINES CORP.

European Appl. 5,163

Pb is applied to a Si-based semiconductor base and the bulk of the metal converted to a Pt silicide barrier layer. Excess Pt is removed by etching in a noble gas atmosphere containing a small amount of O₂ or N₂ to increase the differential between the Pt and PtSi etching rates.

TEMPERATURE MEASUREMENT

Thermocouple System for a Glass Fibre Bushing

NITTO BOSEKI CO. LTD.

U.S. Patent 4,167,403

Metal migration between the leads of a Pt:Pt-Rh thermocouple used to monitor the temperature of a fibre glass bushing is prevented by locating the leads closely adjacent to the bushing walls, so that their temperature is the same as that of the bushing over their whole length. Such a location maintains calibration of the thermocouple for the life of the bushing.

Reductive-Resistant Glazes

JOHNSON MATTHEY & CO. LTD.

French Appl. 2,408,823

A temperature sensitive element is described for use in an electrical resistance thermometer. It consists of a non-conducting support and a vitreous layer filled with conducting particles, such as Ru, Rh, Pd, Ir, Pt, Au, Ag, Fe, Ni, Co or Cu. The vitreous layer is reduction resistant. Optionally an overglaze can also be applied to the vitreous layer. It may also be reduction resistant.

MEDICAL USES

Application of Dental Ceramics to Metal Substrates

MIELE & CIE. G.m.b.H. & CO. *British Patent* 1,557,047

Pt, Pd, Au alloy and base metal substrates used in dentistry are subjected to Zn galvanisation prior to electrophoretic coating with ceramic to produce coatings of even thickness. The amount of galvanisation is adjusted so that oxidation during the subsequent coating process converts all the Zn to Zn oxide.