

μ - Chloro - μ - hydrido - dichlorobis(pentamethylcyclopentadienyl)di-rhodium and -iridium as Homogeneous Hydrogenation Catalysts

C. WHITE, D. S. GILL, J. W. KANG, H. B. LEE and P. M. MAITLIS, *J. Chem. Soc., D, Chem. Commun.*, 1971, (14), 734-735

The hydrido complexes $[\{M(C_5Me_5)_2HCl\}_2]$ (M=Rh,Ir) react readily with 1,3-dienes to give enyl complexes. They are also good catalysts for the homogeneous hydrogenation of olefins.

Effect of Hydroperoxides on the Isomerisation of Olefins Catalysed by a Ruthenium(II) Complex

J. E. LYONS, *J. Chem. Soc., D, Chem. Commun.*, 1971, (11), 562-563

The rate of olefin isomerisation catalysed by $RuCl_2(PPh_3)_3$ is greatly accelerated in the presence of small amounts of hydroperoxides which convert the Ru complex into a catalytically active compound having a CO ligand.

Homogeneous Hydrogenation of Mono- and Diolefins in the Presence of Complexes of Ruthenium with N-Phenylalanine

E. F. LITVIN, L. KH. FREIDLIN, K. G. KARIMOV, M. L. KHIDEKEL' and V. A. AVILOV, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1971, (7), 1539-1541

Ru complexes of N-phenylalanine are more selective catalysts for paraffin formation during diene hydrogenation than Ru/C.

ELECTRICAL AND ELECTRONIC ENGINEERING

Microstructures of Sputtered Platinum Silicide Films

H. N. S. LEE, F. B. KOCH and W. R. COSTELLO, *Extended Abstr., 139th Natl. Mtg., Electrochem. Soc.*, 1971, (May), 171-173

The effects of sputtered deposition variables on the microstructures of PtSi films were studied. Substrate temperature is a dominant factor in determining surface microstructure; higher substrate temperatures produce smoother film surfaces. Pt whisker growth was observed in samples prepared with no continuous back sputtering. Annealing at 500°C is required to convert all the Pt to PtSi.

TEMPERATURE MEASUREMENT

Modern Resistance Thermometry

W. FALLON, *Instrum. Prac.*, 1971, 25, (7), 400-405

The capability of Pt resistance sensor systems is reviewed. The reasons for using Pt, sensor construction, accuracy and resistance bridge networks are discussed. Within their temperature range of application, Pt resistance sensors are the most accurate method of sensing temperature available at present.

NEW PATENTS

METALS AND ALLOYS

Platinum Group Metal Alloys

JOHNSON MATTHEY & CO. LTD.

British Patent 1,238,013

German Offen. 1,758,549

Pt group metals, particularly Rh, Pt and Pd or their alloys, are dispersion strengthened by the addition of up to 20 at.% of at least one of the following: a lanthanide, Sc, Ti, V, Y, Zr, Hf and Ta.

Resistance Alloys

JOHNSON MATTHEY & CO. LTD.

U.S. Patent 3,561,956

Resistance wires having a high electrical resistivity are made from alloys of 74-98.5 wt.% Pd, 1-15 wt.% V and 0.5-11 wt.% Mo. From 0.5 to 8 wt.% Au may also be present.

Sheathed Metals

JOHNSON MATTHEY & CO. LTD.

German Offen. 1,621,254

A refractory metal or alloy article (not Mo or W)

is sheathed in a Pt group metal or alloy, optionally with an intermediate barrier layer of, for example, a rare earth metal carbide. Applications are stated to be stirrers, crucibles, dies etc., in contact with molten glass. This corresponds to *British Patent* 1,190,266.

Palladium-Vanadium Alloy

JOHNSON MATTHEY & CO. LTD.

German Offen. 1,758,310

An alloy of high specific resistance and low temperature coefficient of resistance has the composition 74-98.5 wt.% Pd, 1-15 wt.% V and 0.5-11 wt.% Au, Mo and/or Al.

Dispersion Hardened Materials

DEUTSCHE GOLD- UND SILBER-SCHNEIDANSTALT

German Offen. 1,783,074

Dispersion hardened materials based on Pt metals or Au alloyed with metals and other elements such as Zr, are produced in two stages. In the first stage the material is soaked at 300-800°C. During the second stage it is subjected to oxidative treatment at 800-1400°C.

Alloy for Contact with Molten Glass

JOHNSON MATTHEY & CO. LTD.

German Offen. 2,027,558

An alloy for use in contact with molten glass contains 9–25 wt.% Rh, 1–4 wt.% Au and the remainder Pt. This corresponds to *Dutch Appl.* 70,08,179

CHEMICAL COMPOUNDS

Preparation of Ruthenium Carbonyl

IMPERIAL CHEMICAL INDUSTRIES LTD.

U.S. Patent 3,561,924

A process for the preparation of Ru_3CO_{12} consists of reacting a liquid solution of a Ru salt, an alkali metal or alkaline earth metal compound of an organic acid or of an enolisable compound with CO and H_2 .

Ruthenium Carboxylates

JOHNSON MATTHEY & CO. LTD.

German Offen. 2,034,908; *French Patent* 2,055,059

A new composition of matter is a Ru carboxylate of formula $Ru_2(OCOR)_4$, where R is an optionally substituted alkyl or aryl group. It is produced by heating together a soluble Ru salt, a soluble carboxylate and the corresponding carboxylic acid, e.g., acetic acid. The compounds may be stabilised by complexing them with pyridine or a phosphine.

ELECTROCHEMISTRY

Platinum-plated Electrode

IMPERIAL CHEMICAL INDUSTRIES LTD.

British Patent 1,237,077

A Ti support, electroplated with Pt, is used as anode in the electrolysis of NaCl.

ELECTRODEPOSITION AND SURFACE COATINGS

Electrodeposition of Ruthenium

INTERNATIONAL NICKEL CO. INC.

U.S. Patent 3,576,724

Ru complex compounds are produced in which the anion has the general formula $[Ru_2N(H_2O)_x Y_y]^{z+}$ where Y is a chloro or bromo group, x is 2, 3 or 4, x–y is 10 and z is 5–x and the cation is preferably monovalent, e.g., NH_4^+ , Li, Na or K. A plating bath is prepared using the Ru complex compounds in aqueous acidic solution.

Electrodeposition of a Bright Platinum-Rhenium Alloy

G. HAENSEL and A. ERBEN

East German Patent 73,435

Bright Pt-Re alloy deposits are obtained from fluoroborate baths containing 20g $Pt(NH_3)_2(NO_2)_2$, 12g ammonium perrhenate, 50g HBF_4

and 100g $NaBF_4$ per litre. This gives at 80°C and 2.5 A/dm² a bright adherent deposit 7.5μ thick containing 5% Re and having 230 kg/mm² Vickers hardness.

HETEROGENEOUS CATALYSIS

Ammonia Dissociation Catalyst

GENERAL ELECTRIC CO. *British Patent* 1,229,858

A method for dissociating NH_3 using a heated catalyst comprising one of Ru, Rh, Pd, Os, Ir, Pt or their alloys is described. O_2 is premixed with NH_3 to the extent of 5–21 wt.% and the initial reaction is used to heat the catalyst bed to its operating temperature of 500°C. Ir and Ir alloys are preferred catalysts.

Dehydrogenation Catalyst

UNIVERSAL OIL PRODUCTS CO.

British Patent 1,231,151

Olefins are obtained by dehydrogenation of 6–20 C normal paraffins in the presence of a Pt group metal supported on Al_2O_3 and impregnated with an alkali or alkaline earth metal compound. Preferably one of As, Sb, Bi, S, Se or Te or their compounds is also present. An example of use is a feedstock for detergent manufacturer.

Purification of Exhaust Gases

UNIVERSAL OIL PRODUCTS CO.

British Patent 1,231,276

Exhaust gases are passed over Al_2O_3 which has been impregnated with an alkaline earth metal compound and a solution containing a dicarboxylic acid and a catalyst metal (e.g. Pt).

Dewaxing Catalyst

CHEVRON RESEARCH CO. *British Patent* 1,231,970

Waxy hydrocarbon oil is dewaxed by reaction with H_2 in the presence of porous Al_2O_3 with 0.2–1 wt.% of Pt and 0.1–2 wt.% of Re.

Reforming Catalyst

MOBIL OIL CORP.

British Patent 1,232,472

Hydrocarbons in the naphtha boiling range are reformed over a catalyst containing 0.3–0.45 wt.% of Pt.

Manufacture of Nitric Acid

HERCULES INC.

British Patent 1,232,903

NH_3 is oxidised to HNO_3 with atmospheric O_2 over a Pt–Rh catalyst.

Hydrogenation Catalyst

ESSO RESEARCH AND ENGINEERING CO.

British Patent 1,234,960

Isoparaffinic jet fuel is obtained from a quality-deficient kerosene fraction by isomerisation and hydrogenation in the presence of a catalyst which is Pt/ Al_2O_3 .

Hydrogenation Catalyst

UNIVERSAL OIL PRODUCTS CO.

British Patent 1,236,341

S-containing pyrolysis gasoline is hydrogenated over Pd/lithiated Al_2O_3 .

Isomerisation Catalyst

BRITISH PETROLEUM CO. LTD.

British Patent 1,236,533

Alkylaromatic hydrocarbons, particularly xylenes, are isomerised in the presence of a catalyst which consists of a decationised mordenite carrying a hydrogenating metal such as Pt, Pd or Ag.

Production of Nitric Oxide

INSTYTUT NAWOZOW SZTUCZNYCH

British Patent 1,236,819

Nitric oxide (NO) is obtained by the oxidation of NH_3 with O_2 and water vapour at 750–900°C first with a Pt and then with a metal oxide catalyst. The first catalyst is a gauze of Pt or Pt-Rh alloy, the second a mixture of Cr_2O_3 and Fe_3O_4 with graphite and an activator which is an oxide of a metal, e.g. Cu or Ag.

Hydrogenation Catalyst

CONTINENTAL OIL CO. *British Patent 1,236,890*

Ziegler alcohols are converted to normal aliphatic alcohols by hydrogenation in the presence of a catalyst which may be Rh or Ru on Al_2O_3 or Pt/C.

Dehydrogenation Catalyst

UNIVERSAL OIL PRODUCTS CO.

British Patent 1,237,550

Linear detergent alkylate is obtained by dehydrogenation of a normal paraffin feedstock in the presence of a Pt group metal.

Reforming Process

ANTAR PETROLES DE L'ATLANTIQUE

British Patent 1,238,042

Petroleum reforming is carried out at a controlled temperature in an elongated reactor. Pt/ Al_2O_3 is distributed in several separate zones in the reactor.

Catalytic Reforming of Hydrocarbons

UNIVERSAL OIL PRODUCTS CO.

U.S. Patent 3,562,147

A continuous process for the catalytic reforming of a gasoline fraction to produce a high octane reformat stream uses a Pt group metallic component, a Re component, a halogen component, and a S component, all of which are composited with an Al_2O_3 carrier material.

Hydroforming with a Promoted Iridium Catalyst

ESSO RESEARCH & ENGINEERING CO.

U.S. Patent 3,567,625

In a hydroforming process the catalyst is Ir

and a metal selected from Au, Cu or Ag supported on a high surface area support.

Method of Removing Nitrogen Oxides from Gases

W. R. GRACE & CO.

U.S. Patent 3,567,367

The catalytic reduction of N oxides in tail gas from HNO_3 synthesis is improved when water is added to the tail gas prior to and after final reduction so as to give increased reduction, longer catalyst life, and increased energy available for recovery in the treated effluent. The catalysts may be Pt, Rh or Pd.

Hydrocarbon Conversion Process

TEXACO INC.

U.S. Patent 3,567,796

A hydrocarbon conversion process is described in which a catalyst consisting essentially of (1) Al_2O_3 , (2) a metal selected from Ru, Rh, Pd and Pt and (3) Cl_2 or Br_2 is used. At least a part of the Cl_2 or Br_2 is introduced into the catalyst by contacting a composite of Al_2O_3 and the metal at elevated temperature with a selected organic compound in the presence of Cl_2 or Br_2 .

Hydrocarbon Conversion Process

UNIVERSAL OIL PRODUCTS CO.

U.S. Patent 3,574,092

A catalytic composite consists of a Pt group metallic component and a Tc component combined with a carrier material containing Al_2O_3 and a finely divided crystalline aluminosilicate. An example of the catalytic composite is a combination of 0.01–1.0% Pt and 0.01–1.0% Tc with a γ - Al_2O_3 carrier material having 0.5–20 wt.% of the H form of mordenite uniformly distributed.

Hydrocracking Catalyst

CHEVRON RESEARCH CO.

U.S. Patent 3,576,736

A hydrocracking catalyst has a crystalline zeolite molecular sieve cracking component, 0.01–2.0% of a hydrogenating component selected from Pt, Pd, Rh, Ru, Ir and their compounds and 0.01–5.0% of a Au or Au compound cracking component.

Dehydrogenation Catalyst

UNIVERSAL OIL PRODUCTS CO.

U.S. Patent 3,576,766

Hydrocarbons are dehydrogenated by contacting them with a composite containing catalytically effective amounts of a Pt group component, a Re component, and a Sn component with a porous carrier material. A specific example is a combination of Pt, Re, Sn and an alkali or alkaline earth component with an Al_2O_3 carrier material.

Platinum Catalyst

INSTITUT FRANCAIS DU PETROLE, DES CARBURANTS ET LUBRIFIANTS

French Patent 1,588,196

A catalyst for a hydrocarbon process consists of

Pt/Al₂O₃ obtained by impregnating an Al₂O₃ gel with a halogen acid and then cooling suddenly to retain the halogen.

Hydrogenated Phthalic Acids

POLYCARBON CHEMIE-G.m.b.H.

German Offen. 1,593,226

A low melting mixture of hydrogenated acids is obtained by the isomerisation of tetrahydrophthalic anhydride in the presence of a supported Pd, Pt and/or Ru catalyst.

Carboxylic Acid Production

KNAPSACK A.G.

German Offen. 1,618,589

Carboxylic acids are produced by the oxidation of 2-6C aldehydes in the presence of a supported catalyst containing Pd metal, Pd oxide and/or a Pd salt and at least one other component which may be another Pt metal, Ag or Au.

Oxidation Catalyst

JOHNSON MATTHEY & CO. LTD.

German Offen. 1,668,202

In a continuous process for the preparation of gluconic acid or glucosaccharic acid, an aqueous solution of glucose containing Na or K carbonate or bicarbonate is contacted in a trickle column with an O₂-containing gas in the presence of a supported Pt group metal. This corresponds to *British Patent* 1,208,101.

Purification of Gases

JOHNSON MATTHEY & CO. LTD.

German Offen. 2,045,487

N oxides are removed from a gas containing O₂ and at least one N oxide by mixing the gas with a gaseous reducing fuel and passing it, at a temperature above the ignition temperature, over a catalyst. The catalyst consists of an inert support coated or impregnated with a mixture of Pt and 20-50 wt.% Rh. The inert support may be in the form of a ceramic honeycomb. This corresponds to *French Patent* 2,061,385.

Removal of Organic Pollutants from Waste Gases

JOHNSON MATTHEY & CO. LTD.

German Offen. 2,045,488

Organic compounds (including CO and hydrocarbons) which are present in waste gases and which would otherwise cause atmospheric contamination are oxidised to CO₂ and H₂O by passage, together with O₂ over a supported mixture or alloy containing 50-80 wt.% Pt and 50-20 wt.% Rh.

Catalytic Reactions

JOHNSON MATTHEY & CO. LTD.

German Offen. 2,047,748; *Dutch Appl.* 70.14,341

Solid catalysts for hydrogenation, hydroformyl-

ation or carbonylation are obtained by treatment of an inert solid porous support with a solution of a complex of an hydridocarbonyl bis- or tris-(trisubstituted phosphine)Rh complex. Alternatively, a solution of a halogen- or pseudohalogen-containing complex of Rh in which at least one stabilising donor ligand is present may be used.

Platinum-Rhenium-Germanium Catalysts

UNIVERSAL OIL PRODUCTS

Dutch Appl. 70.09,855

An Al₂O₃-supported catalyst contains 0.05-1 wt.% Pt, 0.05-1 wt.% Re, 0.05-2 wt.% Ge and 0.5-1.5 wt.% Cl₂. The catalyst is used for reforming, isomerising and hydrocracking.

Catalytic Hydroformylation

JOHNSON MATTHEY & CO. LTD.

Dutch Appl. 70.16,532

Organic compounds are hydroformylated in the vapour phase with carbon monoxide and hydrogen in the presence of a Rh hydride carbonyl bis- or tris(trisubstituted phosphine, arsine or stibine) deposited upon a solid support as catalyst. The solid support may be a ceramic honeycomb or a porous organic polymer.

HOMOGENEOUS CATALYSIS

Hydrogenation Catalyst

IMPERIAL CHEMICAL INDUSTRIES LTD.

British Patent 1,232,015

Unsaturated organic compounds are selectively hydrogenated in the presence of a soluble compound of Rh, Pd, Os, Ir or Pt and an organic polar hydroxylic solvent.

Catalyst for Production of Aromatic Isocyanates

OLIN CORP.

British Patent 1,232,863

A nitro-compound can be converted directly to the corresponding isocyanate by reaction with CO in the presence of Pd or Rh halide or oxide with at least one oxide of V, Mo, W, Nb, Cr or Ta. See also *British Patent* 1,232,865.

Catalyst

ASAHI KASEI K.K.K.

British Patent 1,237,510

Dimethylstyrene is obtained by reaction of xylene with C₂H₄ and O₂ in the presence of a lower aliphatic carboxylate of Pd activated with an oxide or lower aliphatic carboxylate of a metal such as Cu or Ag.

Aliphatic Acid and Ester Production

UNION OIL CO.

U.S. Patent 3,573,332

The telomerisation of C₂H₄ in the presence of dihalo- and trihaloacetic acids and their esters is catalysed by Pd(CN)₂ to produce halogenated long chain fatty acids. In a typical reaction C₂H₄ is contacted with chloroacetic acid in the presence of Pd(CN)₂.

Hydrogenation of Unsaturated Carboxylic Acids

JOHNSON MATTHEY & CO. LTD.

U.S. Patent 3,574,734

A process for the hydrogenation of water-soluble, unsaturated lower aliphatic hydrocarbon carboxylic acids comprises mixing an aqueous solution of the unsaturated acid with a catalyst in the form of an ionic water-soluble ammino compound of Rh, the cation of which has the formula $[\text{HRh}(\text{NH}_3)_5]^{2+}$ or $[\text{HRh}(\text{NH}_3)_4\text{H}_2\text{O}]^{2+}$.

Rhodium Complexes

INSTITUT FRANCAIS DU PETROLE

French Appl. 2,041,776

New hydroformylation catalysts are Rh carbonyl complexes of As-, Sb- or P-containing ligands, e.g. the reaction product of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ with dipiperidinophenylphosphine.

Transition Metal Carboxylate Catalysts

JOHNSON MATTHEY & CO. LTD.

German Offen. 2,034,909

Transition metal compounds useful for catalysis are obtained by complexing a Pt group metal or other transition metal carboxylate, thiocarboxylate or dithiocarboxylate with a stabilising ligand. In one example a Rh benzoate catalyst is stabilised by a phosphine. Protonation of these compounds with strong acids produces species of the type M_2^{4+} (where M is the transition metal used) showing a high activity for the catalysis of hydrogenation and other reactions. Preferred Pt group metals are Rh and Ru. This corresponds to *French Patent 2,055,060*.

FUEL CELLS AND BATTERIES

Fuel Cell Electrode

VARTA A.G.

British Patent 1,231,934

A catalyst electrode for the electrochemical conversion of alcohols and hydrocarbons in fuel cells consists of a porous supporting body (e.g. Raney Ni) with a surface layer of 70–99% Pt, Pd or a mixture and 1–30% Pb.

CHEMICAL TECHNOLOGY

Coated Titanium Electrodes

P.P.G. INDUSTRIES INC. *British Patent 1,231,995*

An anode for electrolysis of aqueous alkali metal chloride solutions is obtained by (1) coating a Ti base with a mixture of thermally decomposable compounds of Ti and a Pt group metal such as Ti and Ru resins, and (2) heating to produce the metal.

Hydrogen Pumping Apparatus

GENERAL ELECTRIC CO.

U.S. Patent 3,568,410

A gas pump of simplified, sturdy construction employs Pd maintained at a high temperature to

permit efficient evacuation of gas from a region of low pressure to a region where partial pressure of the gas is several orders of magnitude higher.

Electrochemical Production of Olefin Oxides

FARBENFABRIKEN BAYER A.G.

German Offen. 1,618,405

Olefin oxides are produced electrochemically in a cell, the parent olefin being converted to halohydrin and then to olefin oxide. The cell anode consists of a Ti core coated with an oxide of one or more of Pt, Pd, Ir, Ru and Rh.

ELECTRICAL AND ELECTRONIC ENGINEERING

Thorium Film Cathodes

SIEMENS A.G.

British Patent 1,234,905

A Th film cathode for an electrical discharge vessel is formed from a cathode blank of a high-melting metal (preferably W) containing ThO_2 . The formed blank is then coated with a layer of metallic Rh, Os, Pt, Ir or Re.

Semiconductor Device

FUJISU LTD.

British Patent 1,238,747

In a semiconductor device the terminal block consists of a layer of Cr, Mo, V, Ti, Zr or Hf, covered with a layer of Pt, Pd or Rh.

Pattern Deposit by Laser

INTERNATIONAL STANDARD ELECTRIC CORP.

U.S. Patent 3,560,258

A technique for forming an interconnection pattern on a substrate consists of placing opposite the substrate a film of a vaporisable material disposed on a glass plate. A beam of intense radiant energy scans the metallic film through the glass plate to evaporate selectively portions of the film which deposit on the semiconductor substrate in accordance with the desired pattern. Pt is the preferred vaporisable material.

Ceramic Electrical Resistors

E.I. DU PONT DE NEMOURS & CO.

U.S. Patent 3,565,682

Pd oxides of formula PdMO_2 , where M is Co, Cr, Rh or a mixture of Cr with Rh, can be mixed with a vitreous enamel or glass frit and optionally other additives to form ceramic resistor compositions. Such compositions are applied to a ceramic dielectric substrate and fired, forming the conductive coating of a ceramic electrical resistor.

Cermet Resistor Composition

ALLOYS UNLIMITED INC.

U.S. Patent 3,573,229

An improved resistance composition has a conductive fraction made of Au, Ag or Pt mixed with Ir or Ru oxide. The frit content is not more than about 78%.