

Mechanism of the Homogeneous Hydrogenation of Olefins Catalysed by Chlorocarbonyltris (triphenylphosphine) iridium (I) with and without Basic Cocatalysts

M. G. BURNETT, R. J. MORRISON and C. J. STRUGNELL, *J. Chem. Soc., Dalton Trans.*, 1973, (7), 701-708

In a polar solvent, the rate of hydrogenation of olefins catalysed by $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ increased to a maximum during an induction period. In toluene, or when a radical inhibitor was added, the induction period did not occur. The delay was attributed to radical side chain reactions. Basic cocatalysts in polar solvents converted the catalyst to $\text{IrH}_3(\text{CO})(\text{PPh}_3)_2$. The hydrogenation mechanism is discussed in terms of an Ir-olefin intermediate.

Selective Hydrogenation of 1,5,9-Cyclododecatriene to Cyclododecene Catalysed by Ruthenium Complexes

D. R. FAHEY, *J. Org. Chem.*, 1973, 38, (1), 80-87

The selective homogeneous hydrogenation of 1,5,9-cyclododecatriene (CDT) to cyclododecene—important in the synthesis of polyamide monomers—is catalysed by Ru complexes, especially $(\text{PPh}_3)_2(\text{CO})_2\text{RuCl}_2$ which gives yields of 98.5% at 125-160°C, 100-200 lb/in² H₂; it can be formed directly from RuCl_3 , PPh_3 and CO in situ. At least 32,100 mol of CDT can be selectively hydrogenated per mole of $(\text{PPh}_3)_2(\text{CO})_2\text{RuCl}_2$. Rate measurements suggest the hydrogenation is first order in olefin and catalyst.

NEW PATENTS

METALS AND ALLOYS

Cladding Alloys

LEACH & GARDNER CO. *British Patent* 1,310,082
Cladding alloys, especially for a core of Be-Cu, contain 40-60 wt. % Au, 9.6-14.4% Pd, 4.8-7.2% Ag and Ni, 19.2-28.8% Cu and 1.6-2.4% Zn. They replace more expensive Au, Ag and Pt alloys, e.g. in spring contacts.

Palladium Alloy-Silver Alloy Composite Materials

MATSUSHITA ELECTRIC INDUSTRIAL CO. LTD.
British Patent 1,312,151

A composite material intended for electrical contacts consists of a Pd alloy sheet and an Ag alloy sheet bonded together using a Ni-Cu sheet at 720-850°C and rolled to required thickness.

Graphite/Noble Metal Mixtures

BRITISH PETROLEUM CO. LTD.
British Patent 1,312,273

A mixture of graphite and Pt, Au or Ag is obtained

CHEMICAL TECHNOLOGY

The Preparation and Purification of Americium Metal by Evaporation

J. C. SPIRLET and W. MÜLLER, *J. Less-common Metals*, 1973, 31, (1), 35-46

In order to redetermine its physical and chemical properties several grams of ²⁴¹Am were prepared by thermal dissociation of Pt_3Am , formed by the reduction of AmO_2 with ultrapure H₂ in the presence of Pt powder. The Am metal was purified by sublimation at 1100°C, 10⁻⁶ Torr. Metal impurities were analysed by emission spectrography, and O, N and H by vacuum hot extraction. Amounts of O, N and H were ≤250, 50 and 20 p.p.m. respectively.

TEMPERATURE MEASUREMENT

Temperature Control Using a Platinum Resistance Sensor

G. D. BRABSON and A. A. FANNIN, *Rev. Sci. Instrum.*, 1973, 44, (3), 338

Improved control of a constant temperature bath is achieved using a Pt resistance thermometer in a resistance bridge to generate an error signal proportional to the difference between actual and desired temperatures. The error signal, ~0.4mV/°C, is ten times the magnitude of the Chromel-Alumel thermocouple signal it replaces.

by grinding a natural or synthetic graphite with Pt, Au or Ag in an organic liquid to give a surface area of at least 5 m²/g. This mixture can be used in lubricants.

Platinum Metal Alloys

JOHNSON MATTHEY & CO. LTD.
U.S. Patent 3,709,667

Dispersion-strengthened Pt group metals and alloys are produced by introducing an oxide refractory precursor such as Zr as an alloying additive. The alloy formed is converted to powder, cold worked, oxidised to give an oxide in the powder and then compacted and sintered.

Sprayed Metal Articles

JOHNSON MATTHEY & CO. LTD.
Dutch Appl. 71.11161

Metal articles are produced by arc, flame or plasma spraying Pt or Pt alloy droplets at a cold target to form a coherent layer of individual particles which are then mechanically worked to a mass.

CHEMICAL COMPOUNDS

Benzodiazepine Derivatives

F. HOFFMANN-LA ROCHE A.G.

British Patent 1,304,707

Benzodiazepine derivatives carrying a ring CH_2 group may be oxidised to the corresponding derivatives having a ring carbonyl group using RuO_4 .

Rhodium-Tellurium Oxide

SOLVAY & CIE.

British Patent 1,306,057

A new compound, Rh_2TeO_8 , may be produced by milling the two oxides together. It is useful as an oxidation catalyst and electrochemical electrode material.

ELECTROCHEMISTRY

Electrode Production

BADISCHE ANILIN- & SODA-FABRIK A.G.

British Patent 1,303,865

A Ti, Zr or other stable core is coated with an oxide mixture of at least one Pt group metal and at least one Si, Ge or Sn oxide and fired at 200–1200°C. Ru/Si oxides form an adherent electrode coating.

Electrolytic Cells

CALIFORNIA INSTITUTE OF TECHNOLOGY

British Patent 1,304,011–1,304,012

A gas chromatograph system has an electrolytic cell in which both anode and cathode only conduct H when hot. Preferably both electrodes are formed from, or incorporate, Pd or Pd alloys such as Pd-Ag.

Electrolysis Electrodes

IMPERIAL CHEMICAL INDUSTRIES LTD.

U.S. Patent 3,701,724

Electrodes used in electrochemical processes are coated with a minor amount of a Pt group metal oxide and a major amount of an Sn, Sb or Ge oxide, e.g. Sn and Ru oxides.

ELECTRODEPOSITION AND SURFACE COATINGS

Chemical Plating

KOLLMORGEN CORP.

British Patent 1,306,201

A sensitizer solution for chemical metal plating contains a double metal complex of a Group VIII or IB noble metal, a Group IV metal and an anion, e.g. a Ru-Sn chloride complex.

Two Stage Chemical Plating

CROWN CITY PLATING CO. *British Patent 1,307,927*

Plastics articles are etched and sensitised with a Pd salt in the usual way. A thin strike coating of Cu is applied and is followed by a heavy coating from

an inhibited bath that would not plate on to the original Pd nuclei.

Chemical Plating of Uranium

U.S. ATOMIC ENERGY COMMISSION

U.S. Patent 3,700,482

U surfaces are degreased, pickled and sensitised with PdCl_2 before chemical plating with Ni.

Electrode Pattern

BELL TELEPHONE LABORATORIES INC.

U.S. Patent 3,700,569

Electrode patterns are produced by metallising with Pt, oxidising the Pt surface, masking it and then applying Au.

LABORATORY APPARATUS AND TECHNIQUE

Gas Analysis

CALIFORNIA INSTITUTE OF TECHNOLOGY

U.S. Patent 3,701,632

Pd membranes permeable to H_2 are used in the analysis of gas streams.

Humidity Sensor

HONEYWELL INC.

U.S. Patent 3,703,697

A relative humidity sensor consists of a noble metal electrode coated with an oxide of Fe, Co or Ni.

Carbon Dioxide Sensor

GENERAL ELECTRIC CO.

U.S. Patent 3,705,088

A sensor for CO_2 has a Pd/PdO surface and a Ag/Ag halide surface.

Hydrogen Ion Sensor

GENERAL ELECTRIC CO.

U.S. Patent 3,709,810

An H^+ selective sensor has an electrode with a Pd surface coated with PdO.

Hydrogen Diffusion Unit

JOHNSON MATTHEY & CO. LTD.

French Appl. 2,130,582

A diffusion unit of two superimposed metal foils, e.g. Ag/Pt, is described in which at least one foil or preferably both, are corrugated. A wire helix is situated in each corrugation to prevent collapse under high pressures and to facilitate diffusion and collection of H_2 .

JOINING

Brazing Alloy

WESTERN GOLD & PLATINUM CO.

U.S. Patent 3,702,763

A high temperature alloy for brazing Ti alloy systems contains 1–20% Pd, 3–10% Ga and balance Ag, e.g. 87%Ag, 10%Pd, 3%Ga. A preferred range contains 7–15% Pd and 5–9% Ga.

HETEROGENEOUS CATALYSIS

Hydrofining Combined Process

ESSO RESEARCH & ENGINEERING CO.

British Patent 1,305,054

"Hydrodesulphurfining" is carried out in a recycle process in which the preferred catalysts are Pd, Pt, Mo, Ni and/or Co on Al_2O_3 or SiO_2 .

Aromatisation Catalyst

ASAHI KASEI KOGYO K.K. *British Patent 1,305,137*

Aromatic compounds are produced from C_2H_4 , etc., and H_2 at 300–650°C in the presence of a supported mixture of Pt, Pb and at least one of Li, Na, K, Rb, Cs, Ca, Mg, Be, Zn, Sr, Ba, Cd, Hg, Ge, Sn, Bi, Cr, Mo, W, U, Re, Rh, Ru, Pd, Os or Ir.

Acetic Acid Production

AJINOMOTO CO. INC. *British Patent 1,306,863*

CH_3COOH is produced from CO, CH_3OH and H_2 in the presence of a transition metal catalyst and a halogen-containing co-catalyst, e.g. Rh/C and molecular halogen.

Acetylene Removal from Olefins

POLYMER CORP. LTD. *British Patent 1,307,554*

Olefines are removed from olefinic feedstocks by contact with a catalyst containing a Group I–III metal hydride or organic compound and a transition metal compound. Rh, Pd, Os and Pt are claimed specifically.

Nitrogen Dioxide Removal from Gases

BADISCHE ANILIN- & SODA-FABRIK A.G.

British Patent 1,308,383

NO_2 is removed from gases by reacting it with CO in the presence of Pd and/or Pt deposited on Al_2O_3/SiO_2 .

Water Vapour in Gases

AIR PRODUCTS & CHEMICALS INC.

British Patent 1,309,098

A controlled amount of H_2O vapour in a carrier gas is produced by reacting measured amounts of H_2 with an oxidising agent in the gas. The oxidising agent may be air or N_2O ; Pt group metals catalyse the formation of H_2O .

Inhibition of Hydrogenolysis

ESSO RESEARCH & ENGINEERING CO.

British Patent 1,309,862

In the catalytic conversion of hydrocarbons using Pt group metal catalysts, unwanted hydrogenolysis to light products is avoided by adding a Group IB metal to the catalyst, e.g. Cu or Ag can be used with Ru on SiO_2 .

Electrically Non-conductive Carbon

FARBWERKE HOECHST A.G.

British Patent 1,310,175

Non-conducting C is produced by dehydrogenating a polycycloaliphatic compound in the presence of a Pt, Ni or Pd catalyst.

White Mineral Oil Production

ATLANTIC RICHFIELD CO. *British Patent 1,310,320*

A lubricating oil distillate is converted to a white mineral oil using a hydroisomerisation/hydrocracking catalyst and a hydrogenation catalyst, the latter containing a Pt metal.

Lubricating Oil

ATLANTIC RICHFIELD CO. *British Patent 1,311,431*

A high viscosity index lubricating oil is produced by treating a crude with H_2 in the presence of a hydrogenation-hydrocracking catalyst. This catalyst consists of a Pt group metal deposited on a rare earth-exchanged crystalline aluminosilicate.

Hydrocarbon Isomerisation

GULF RESEARCH & DEVELOPMENT CO.

British Patent 1,311,554

More highly branched hydrocarbons are obtained by purifying a feed-stock on a molecular sieve and then contacting it with a supported Pt group catalyst, e.g., a commercial Pt/ Al_2O_3 reforming catalyst.

Synthetic Diamonds

UKRAINSKY ORDENA TRUDOVOGO KRASNOGO

ZNAMENI NAUCHNO-ISSLED. KONSTRUKTORSTSEKH-

NOLOGICHESKY INSTITUT

British Patent 1,311,641

Diamond synthesis is catalysed by a metal having graphite crystallites dispersed in it. The six Pt metals are suitable catalytic metals.

I.C.E. Exhaust Gas Treatment

UNIVERSAL OIL PRODUCTS CO.

U.S. Patent 3,701,823

I.C.E. exhaust gases are treated in two catalyst stages. The second stage catalyst may be a Pt group metal or Ag and is concerned with CO removal.

Isomerisation Catalyst

UNION OIL CO. OF CALIFORNIA

U.S. Patent 3,706,815

New catalysts for isomerisation processes are Pt group metal chelates of a polyphosphoric acid deposited on a support, e.g. tetramine platinum(II) pyrophosphate on graphite.

Hydrofining-Hydrocracking Catalysts

CHEVRON RESEARCH CO. *U.S. Patent 3,709,814*

A hydrofining-hydrocracking process uses a catalyst consisting of Pd on a molecular sieve and Ni or Co on a $SiO_2-Al_2O_3$ gel support.

Oxidation Catalysts

JOHNSON MATTHEY & CO. LTD.

French Appl. 2,130,310

Catalysts for I.C.E. exhaust gas treatment, NO reduction and reforming reactions are alloys of Pt, 1–50% Rh and 0.01–25% base metal.

High Temperature Catalysts

JOHNSON MATTHEY & CO. LTD.

German Offen. 2,228,909

Articles such as thermocouples or supported catalysts which are for use at high temperatures in reducing or non-oxidising conditions consist of a refractory core coated with a MgO barrier layer and then with a layer of a Pt group metal or alloy. The core may consist of a refractory oxide, carbide, nitride, etc.

Gauze Catalyst

JOHNSON MATTHEY & CO. LTD.

German Offen. 2,239,514

Gas reactions, such as NH_3 oxidation for HNO_3 production, are catalysed by two sets of gauzes. The reactant gases first come into contact with noble metal gauzes, e.g. 10% rhodium-platinum alloy, and then with less volatile catalytic gauzes, e.g., austenitic 21% Ni, 23% Cr stainless steel or a Pt-Ni-Cr alloy.

HOMOGENEOUS CATALYSIS

Synthesis of Octadienyl Alcohols

UNION CARBIDE CORP. *British Patent* 1,307,101

Butadiene and H_2O can be reacted in the presence of a Pt, Pd or Ru complex of a phosphine, diketone, etc., to give octadienol as a direct product.

Aldehyde Production

CELANESE CORP.

British Patent 1,307,346

Olefins are reacted with H_2 and CO to give aldehydes in the presence of a Rh arsine, phosphine or stibine complex, e.g. $(\text{PPh}_3)_2\text{Rh}(\text{CO})\text{Cl}$.

Allyl Carboxylate Isomerisation

TOYO SODA MANUFACTURING CO. LTD.

British Patent 1,308,749

Esters of allyl alcohol are isomerised by certain Pt chlorides, chloroplatinum acids and their salts. The preferred catalysts are PtCl_4 and H_2PtCl_6 and its salts.

Alcohol Production

IMPERIAL CHEMICAL INDUSTRIES LTD.

British Patent 1,309,153

9 C alcohols are produced by reacting butadiene with HCHO in the presence of a Pt or Pd compound. Pd phosphine, acetylacetonate and maleic anhydride complexes are mentioned in the examples.

Olefin Conversion Catalyst

INSTITUT FRANCAIS DU PETROLE, DES CARBURANTS ET LUBRIFIANTS

British Patent 1,309,529

Olefin conversion reactions are catalysed by a mixture of one or more Lewis acids and one or more "carbenometal" compounds having the formula $(\text{L})_m\text{M}=\text{CXY}$, where M is a Group

VI-VIII metal especially Mn, Cr, Mo, W, Fe, Pt, Pd or Ru, L is a N, O, P, As, Sb ligand, halogen, and/or a C-C multiple bond, m is 1-5 and X and Y are 1-30 C hydrocarbons. Thus $(\text{PPh}_3)_2\text{Cl}_2\text{Pd}=\text{C}(\text{OMe})(\text{NHPH})$ can be used with EtAlCl_2 .

Hydroformylation Process

B.P. CHEMICALS LTD.

British Patent 1,312,076

Aldehyde production by olefin hydroformylation is catalysed by a complex of a Group VIII metal other than Fe, Ni, Pd or Pt, e.g. $\text{Rh}(\text{CO})_2(\text{acac})$.

Tetrahydropyran Derivatives

TORAY INDUSTRIES INC. *British Patent* 1,312,138

A compound having a divinyl tetrahydropyran structure is produced from a diene and formaldehyde or higher aldehyde in the presence of a Pd complex, especially a zerovalent or divalent complex such as Pd bisacetylacetonate.

Olefin Carbonylation Process

MOBIL OIL CORP.

U.S. Patent 3,700,706

Olefins are converted to acids and/or esters using a phosphine-complexed Pd salt and a Sn co-catalyst.

Allyl Esters

PHILLIPS PETROLEUM CO.

U.S. Patent 3,700,724

The reaction of allyl halides and carboxylates to produce allyl esters is catalysed by alkali metal or ammonium tetrahalopalladate or tetrahaloplatinate, e.g. K_2PdCl_4 .

Addition to Double Bonds

HERCULES INC.

U.S. Patent 3,700,727

Organic groups are introduced into an ethylenically unsaturated acid, nitrile or ester using an unstable Pd adduct formed in situ, e.g. phenyl Hg chloride and Li_2PdCl_6 act to produce phenyl Pd chloride which introduces phenyl into methyl methacrylate, forming methyl cinnamate.

Aromatic Acid Production

UNION OIL CO. OF CALIFORNIA

U.S. Patent 3,700,729

An aromatic acid is formed from an aromatic compound and CO in the presence of Pd and/or ferric chloride or bromide.

Methyl Ethyl Ketone Production

H. HASEGAWA et al.

U.S. Patent 3,701,810

MEK is produced from n-butene in the presence of Cl^- , Pd^{++} and Fe^{+++} ions.

Olefin Addition Reaction

UNION OIL CO. OF CALIFORNIA

U.S. Patent 3,702,856

C_2H_4 and/or C_3H_6 are reacted with a halogen acid, H_2O and/or a carboxylic acid to give an alkyl halide, alcohol and/or carboxylic acid in the presence of a Pt group metal catalyst, e.g. PdCl_2 .

Organic Phosphorus Compounds

STAUFFER CHEMICAL CO. *U.S. Patent 3,705,214*

Organic P(V) compounds are produced by the reaction of an aryl or vinyl halide with a phosphite in the presence of PdCl₂ or another Pd(II) salt.

Cyclisation Catalyst

UNIVERSAL OIL PRODUCTS CO.

U.S. Patent 3,707,481

Aryl-substituted unsaturated compounds may be cyclised in the presence of a Group VIII metal salt, e.g. Pd acetylacetonate or acetate.

Palladium Complexes in Olefin Dimerisation

PHILLIPS PETROLEUM CO. *U.S. Patent 3,709,955*

Olefin dimerisation is catalysed by a Pd complex and an organic Al compound. Suitable complexes are those of Pd(II) with picoline, cyclohexene, benzonitrile and benzylamine.

Fluorinated Carboxylic Acids and Esters

FARBWERKE HOECHST A.G.

German Offen. 2,137,712

Pd, Ni, Pt, Co, Rh or Ru or their compounds, e.g. a PdCl₂-(PPh₃) complex, are used to catalyse the carboxylation of fluorinated olefins.

FUEL CELLS

Fuel Cell Electrode

GENERAL ELECTRIC CO. *U.S. Patent 3,701,687*

A fuel cell electrode has a catalytic coating containing Pt, Pd and a base metal such as Pb.

CHEMICAL TECHNOLOGY

Needle Electropolishing

ETHICON INC.

U.S. Patent 3,703,452

Surgical steel needles are polished as they are supported in a magnetic film on a Pt, Pd, Rh, Ir or Au anode.

Image Stabilisation

POLAROID CORP.

U.S. Patent 3,704,126

Ag images are stabilised with a noble metal below Ag in the electromotive series, e.g. using a Au, Pt or Pd compound.

Ruthenium-impregnated Graphite

JOHNSON MATTHEY & CO. LTD.

German Offen. 2,228,271

A C or graphite body, preferably porous, is treated to expel gases and then contacted with a solution or suspension of Ru metal or a Ru compound, the solvent or dispersant being subsequently evaporated. The Ru compound may optionally be decomposed. Carbon or graphite particles may be coated by this method and then compressed. The level of impregnation may be predetermined.

ELECTRICAL AND ELECTRONIC ENGINEERING

Ohmic Contacts

R.C.A. CORP.

British Patent 1,307,667

A transistor has semiconductor openings adjacent to the insulated gate which are coated with Pd, Rh, Ru, Os, Ir or Pt, by immersion in a solution of the metal salt acidified with HF, to provide contacts. These can be reinforced with Au.

Silicon Planar Transistors

SIEMENS A.G.

British Patent 1,308,415

A planar Si transistor is made by doping an Si crystal and applying Pt or Pd through a mask. The unit is heated at 350–600°C to form Pt or PtSi.

Semiconductor Devices

T.R.W. INC.

British Patent 1,310,942

A high speed switch semiconductor is doped in some regions with Pt.

Semiconductor Treatment

WESTERN ELECTRIC CO. INC.

British Patent 1,311,048

Boric oxide for use in encapsulating semiconductors is gettered with an alloy of B and Pt or Pd.

Resistance Elements

C.T.S. CORP.

British Patent 1,311,141

Resistance elements are produced from electrically conductive crystals and a vitreous binder which contains an agent for controlling the growth of the crystals. The crystals contain Ru, Ir or a similar element.

Capacitor Cathode

P. R. MALLORY & CO. INC. *British Patent 1,313,400*

A cathode for use in capacitors with strong acid electrolytes has a support of Cu and/or Ag protected with a layer of Au, Pt or Au-Pt alloy.

TEMPERATURE MEASUREMENT

Thermocouple Compensating Leads

JOHNSON MATTHEY & CO. LTD.

French Appl. 2,124,537

A compensating apparatus for a thermocouple, preferably Pt:13%Rh-Pt, comprises two compensating leads, one of which includes at least two insulated conductor limbs, of which one limb is formed from material having thermoelectric properties different from any other conductor limb. The thermoelectric e.m.f. of the combined thermocouple and compensating leads is adjustable.