

Homogeneous Catalytic Hydrogenation and Exchange of Styrenes with Tris(triphenylphosphine)chlororhodium

G. V. SMITH and R. J. SHUFORD, *Tetrahedron Lett.*, 1970, (7), 525-527

Styrene hydrogenation and exchange reactions using this complex were compared with those on metal surfaces. Partial deuteration of styrene in CHCl_3 yielded a novel product distribution. The mechanism of the exchange pattern with ethylbenzene is discussed and the presence of more than one catalyst system is proposed.

Olefin Isomerisation over Tris(triphenylphosphine)chlororhodium

R. L. AUGUSTINE and J. F. VAN PEPPEN, *J. Chem. Soc., D, Chem. Commun.*, 1970, (8), 495-496

Olefin isomerisation over $\text{Rh}(\text{Ph}_3\text{P})_3\text{Cl}$ is dependent on the presence of O_2 in the system and on the solvent used.

The Effect of Solvent on the Dissociation of Tris(triphenylphosphine)chlororhodium

Ibid., 497

Dissociation of $\text{Rh}(\text{Ph}_3\text{P})_3\text{Cl}$ to Ph_3P and $\text{Rh}(\text{Ph}_3\text{P})_2\text{Cl}$ occurs quite readily in C_6H_6 but is completely inhibited by the presence of even small amounts of $\text{C}_2\text{H}_5\text{OH}$.

The Solvent Effect on the Oxidation of Tris(triphenylphosphine)chlororhodium

Ibid., 497-498

$\text{Rh}(\text{Ph}_3\text{P})_3\text{Cl}$ oxidation products varied with the solvents used; C_6H_6 , CH_3OH and $\text{C}_2\text{H}_5\text{OH}$.

Further Studies on Hydridocarbonyltris(triphenylphosphine)rhodium(I). Part I. Nature of Inactivation of Catalytic Reactions

M. YAGUPSKY, C. K. BROWN, G. YAGUPSKY and G. WILKINSON, *J. Chem. Soc., A, inorg. phys. theor.*, 1970, (6), 937-941

Hydrogenations and isomerisations of alkenes using $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ are slowed down and are stopped eventually, especially in dilute solutions,

by decay of the catalyst to the complex $[\text{Rh}(\text{CO})(\text{PPh}_3)_2]_2$, which is inactive.

Part II. Isomerisation of n-Pentenes and Hex-1-ene

M. YAGUPSKY and G. WILKINSON, *Ibid.*, 941-944

Rate studies on the homogeneous isomerisation of pent-1-ene using $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ in C_6H_6 solution showed that initially *cis*-pent-2-ene predominates over the *trans* isomer. *cis*→*trans* isomerisation was slower than conversion of pent-1-ene. Isomerisation to *cis*- and *trans*-pent-2-enes during hydrogenation of pent-1-ene at 1 atm, 27°C, occurs at about the same rate as hydrogenation.

The Homogeneous Ruthenium-catalysed Reduction of Nitrobenzene

F. L'ÉPLATTENIER, P. MATTHYS and F. CALDERAZZO, *Inorg. Chem.*, 1970, 9, (2), 342-345

$\text{Ru}_3(\text{CO})_{12}$, $\text{Ru}(\text{CO})_5$ and $\text{Ru}(\text{acac})_3$ promote homogeneous reduction of $\text{C}_6\text{H}_5\text{NO}_2$ to $\text{C}_6\text{H}_5\text{NH}_2$ by CO and H_2 in good yields and conversions. For $\text{CO}:\text{H}_2 > 1$ the yield of by-product diphenylurea increases with the ratio $\text{CO}:\text{H}_2$. At high $\text{CO}:\text{H}_2$ ratios the stoichiometry is probably $\text{C}_6\text{H}_5\text{NO}_2 + 2\text{CO} + \text{H}_2 \rightarrow \text{C}_6\text{H}_5\text{NH}_2 + 2\text{CO}_2$. The proposed mechanism includes a phenyl-nitrene intermediate stabilised by bonding to Ru in a binuclear complex. This undergoes hydrogenolysis to $\text{C}_6\text{H}_5\text{NH}_2$ or CO insertion and hydrogenolysis to 2,2'-diphenylurea. $\text{Fe}(\text{CO})_5$ is much less active than Ru for the reduction.

ELECTRICAL AND ELECTRONIC ENGINEERING

Palladium Silver Thick Film Conductors

Electroplating Metal Finis., 1970 23, (3), 39

Two Pd-Ag ceramic conductive coatings for thick film microcircuits have been announced. The coatings, intended for the printing of high-quality, low-cost conductors, can be fired (700-1000°C) to give dense films with excellent adhesion, good solder leach resistance and high migration resistance.

NEW PATENTS

METALS AND ALLOYS

Alloy for Pen Points

W. C. HERAEUS G.m.b.H. U.S. Patent 3,480,429

An alloy suitable for use in the casting of pen points contains up to 50% of Os and/or Re, 30-45% Ir, 5-20% Ru, up to 25% of a noble metal, and up to 15% of base metal, e.g. Co.

CHEMICAL COMPOUNDS

Organic Complexes of Platinum or Palladium

BRITISH PETROLEUM CO.

British Patent 1,181,485

Stable compounds of Pt or Pd are reacted with a tertiary phosphine and H_2 in an inert organic solvent to produce organic complexes.

Preparing Palladium-pi-allyl Complexes

W. R. GRACE & CO.

U.S. Patent 3,479,379

A process for preparing a Pd- π -allyl complex by agitating a mixture of a stoichiometric excess of a weakly basic Na salt and a Pd(II) salt olefine complex is described.

Intermetallic Group VIII Compounds

N. V. PHILIPS GLOEILAMPENFABRIEKEN

Dutch Appl. 68. 08,111

Intermetallic compounds of formula $A_xA'_y$, where A and A' are Gp. VIII elements, of which at least one is Fe, Co or Ni, and x and y are whole numbers from 1-4 are described. They are produced in chemically pure intercrystalline form by the reaction of A and A' in which one is present as halide, or halogen is present. In an example Pt, Fe and I_2 are heated together to give $FePt_3$. The products have useful magnetic properties.

ELECTROCHEMISTRY

Recovery of SO_2 from Water Gases

IONICS INC.

British Patent 1,184,768

A cyclic sulphate/bisulphite process is provided, in which part of the sulphate is continuously electrolysed in a cell with an acid-resistant anode, e.g., Pt or a Pt-coated electrolytic valve metal.

Electrolytic Cell for Salt Solutions

MARSTON EXCELSIOR LTD

British Patent 1,184,791

In a cell for electrolysing salt solutions the cathode may be of Pt, and the anode of a porous Pt group metal or of porous Ti, Ta or Nb coated with a Pt group metal.

ELECTRODEPOSITION AND SURFACE COATING

Electroless Deposition of Noble Metals

MOBIL OIL CORP.

British Patent 1,180,891

The substrate is placed in contact with a solution of a π complex of the metal, which is then reduced, e.g., with H_2 , to precipitate the metal. It may be Pd, Pt, Ir, Ru, Rh, Os, Ag, Au or Re.

Deposition of Noble Metals

MOBIL OIL CORP.

British Patent 1,181,912

A metal is deposited on a substrate of colloidal dimensions by contacting the substrate with an anhydrous solution of a compound of the metal to be deposited. The substrate has a surface composed of a metal higher in the electromotive series than the metal to be deposited. The metal to be deposited may be Pt, Pd, Ru, Rh, Ir, or Os.

Electroless Metal Plating on Plastics

MACDERMID INC.

British Patent 1,185,954

A plastics surface, after cleaning, is activated by immersion in a dilute acidified aqueous solution of a noble metal salt, e.g., $PdCl_2$, and then electrolessly plated with Ni or Cu. It may then be electro-plated with Ni or Cu and finally with Ni, brass, Au or Cr.

Electrodes

IMPERIAL CHEMICAL INDUSTRIES LTD

British Patent 1,186,454

Electrodes for use in aqueous metal chloride electrolytes consist of a Ti support on to which is electrodeposited, from a bath containing an aliphatic polybasic hydroxy acid, a layer of Pt.

Multilayer Magnetic Coating

BURTON SILVER PLATING CO.

U.S. Patent 3,479,156

A multilayer magnetic coating has several high coercivity ferro-magnetic thin films alternately disposed with, and separated by, non-magnetic barrier layers. Each barrier layer preferably comprises a metal of the Pt group and, to ensure layer continuity, has a minimum thickness of 500 Å.

Deposition of Platinum-Group Metals

INTERNATIONAL NICKEL CO. INC.

U.S. Patent 3,480,523

A bath for plating Ir, Pd, Pt, Rh and Ru and alloys, consists of an aqueous solution of the bromide salt of the metal and excess HBr.

JOINING

Palladium Copper Contact for Soldering

WESTERN ELECTRIC CO.

U.S. Patent 3,476,531

A circuit contact is composed of a Cu layer on which Pd is deposited so that oxidation of the Cu is prevented. All of the Pd goes into solid solution on the subsequent application of solder to attach a wire lead to the contact. The contact has a base layer of an 80% Ni-20% Cr alloy, a layer of Cu on the base layer having a thickness of at least 12,000 Å, and a layer of Pd on the Cu layer having a thickness of 500-750 Å.

Bonding Platinum Metals

JOHNSON MATTHEY & CO. LTD

U.S. Patent 3,478,415

A method of bonding together a refractory metal part and a Pt group metal part by applying to one surface of one of the parts a barrier layer composed of a mixture of a refractory ceramic material and a metal which is substantially soluble in the Pt group metal is described. The other metal part is applied to the barrier layer and heat and pressure are applied to the assembly to cause the metal

constituent of the barrier layer mixture to diffuse into an alloy with the Pt group metal. This leaves a layer or barrier of refractory ceramic material between and intimately bonded to the refractory metal and Pt group metal parts. Au is a suitable barrier metal.

LABORATORY APPARATUS AND TECHNIQUE

Hydrogen Leak Detector

GENERAL ELECTRIC CO. (NEW YORK)

U.S. Patent 3,479,257

A detector for H₂-containing gases has a substrate of high electrical resistivity with a semi-conducting metal oxide coating, a non-continuous film of an activating Pt, Ir, Rh, Au and/or Pd catalyst deposited on the coating, and electrodes connected to the coating at spaced points. The amount of H₂ in the atmosphere surrounding the detector may be measured by the change in resistivity in the coating.

HETEROGENEOUS CATALYSIS

Hydrogenation Catalysts

IMPERIAL CHEMICAL INDUSTRIES LTD

British Patent 1,178,389

Imines can be prepared by heating the amine salt of a dicarboxylic acid with NH₃ and H₂ in the presence of a catalyst (optionally supported) which may be Pd, Pt, Ru, Rh, Re, Os or Ir.

Hydrocarbon Conversion Catalyst

ESSO RESEARCH & ENGINEERING CO.

British Patent 1,178,594

The catalyst consists of a crystalline aluminosilicate zeolite containing Mn cations, 0.01 to 5 wt% of a Pt group metal or compound (e.g., Pd) and less than 10 wt% of an alkali metal oxide.

Catalyst for Manufacture of Hydroxylammonium Salts

FARBENFABRIKEN BAYER A.G.

British Patent 1,179,119

A noble metal catalyst (optionally supported) is used to catalyse the reaction of NO with H₂ in an aqueous mineral acid solution. It is maintained in an active and selective condition by treatment with O₂. The catalyst may be Ru, Rh, Pd, Os, Ir, or, preferably, Pt. See also *British Patent 1,179,120*.

Detoxicating Exhaust Gas

SANITIZED A.G.

British Patent 1,179,537

The exhaust gas from an internal combustion engine is passed with air through a reaction chamber in which an ultrasonic vibration field is generated. An oxidation catalyst, e.g., CuO₂, 99% MnO₂ + 1% AgO, or Pt may also be provided in the chamber.

Hydrogenation Catalyst

IMPERIAL CHEMICAL INDUSTRIES LTD

British Patent 1,179,706

A hydrogenation catalyst such as Ni, Co, Pt, Pd, Rh, Ru, Ir, Os, or Re optionally supported, is used in the reaction of a dicarboxylic acid with NH₃ and H₂ to form an amine.

Hydrogenation Catalyst

INTERNATIONAL NICKEL LTD

British Patent 1,181,969

A mixture of Pt and Ru (75:25), optionally codeposited on porous carbon, catalyses the hydrogenation of nitrobenzene.

Desulphurisation Catalyst

UNIVERSAL OIL PRODUCTS CO.

British Patent 1,181,982

Black oils are desulphurised in the presence of a SiO₂-supported catalyst which may include Pt, Pd, Ir, Os, Rh, and/or Ru as catalytic metal.

Catalytic Reforming

UNIVERSAL OIL PRODUCTS CO.

British Patent 1,182,571

A reforming catalyst is Pt supported on Al₂O₃.

Reforming Catalysts

UNIVERSAL OIL PRODUCTS CO.

British Patent 1,182,818

A hydrocarbon reforming catalyst consists of a finely divided crystalline aluminosilicate suspended in an alumina matrix and composited with at least one active catalytic component. The catalytic component is a noble metal halide, PtCl₂, for example.

Hydrocarbon Reforming Catalyst

UNIVERSAL OIL PRODUCTS CO.

British Patent 1,182,972

A reforming catalyst consists of a noble metal (e.g., Pt) and a refractory inorganic oxide.

Hydrocarbon Reforming Catalyst

UNION CARBIDE CORP.

British Patent 1,183,000

A reforming catalyst consists of a mixture of a zeolite and a noble metal (e.g., Pt) supported on an inorganic oxide.

Hydrocarbon Reforming Catalyst

ESSO RESEARCH & ENGG CO.

British Patent 1,183,397

The catalyst consists of a mordenite aluminosilicate zeolite containing a noble metal, e.g., Pt or Pd.

Hydrogenation Catalyst

BRITISH PETROLEUM CO. LTD

British Patent 1,184,022

Cyclo-alkyl aromatic hydrocarbons are produced

by high temperature reaction of an aromatic hydrocarbon with H_2 in the presence of a molecular sieve material impregnated with a Group VIII metal, e.g., Pt, Pd, Ru, Rh or Os.

Reforming Catalyst

UNIVERSAL OIL PRODUCTS CO.

British Patent 1,184,196

The catalyst consists of a crystalline aluminosilicate suspended in an alumina matrix and supporting an active catalytic component, e.g., Pt.

Reductive Amination Catalyst

IMPERIAL CHEMICAL INDUSTRIES LTD

British Patent 1,185,310

Imines and diamines are prepared by heating a carboxylic acid with NH_3 and H_2 in the presence of a Ru catalyst, e.g., the metal or its oxide.

Oxidation Catalyst

FARBWERKE HOECHST A.G.

British Patent 1,185,373

Phenyl esters (and phenol) can be produced by reacting C_6H_6 with a saturated aliphatic carboxylic acid and O_2 in the presence of a noble metal, e.g., Rh, Ir and, Pt, Ru or Pd.

Dehydrogenation Catalyst

SHELL INTERNATIONALE RESEARCH MIJ N.V.

British Patent 1,185,813

The catalyst is a calcined, SiO_2 -supported mixture of a Pt metal with Sn and/or Bi.

Hydrocracking Catalyst

BADISCHE ANILIN- & SODA-FABRIK A.G.

British Patent 1,187,075

Petrol or jet fuel is obtained by hydrogenation of high boiling hydrocarbons in the presence of specified ratios, in different stages, of an active catalyst (e.g., Pd, Pt) on aluminosilicate supports.

Cracking Catalyst

UNIVERSAL OIL PRODUCTS CO.

British Patent 1,187,678

Such catalysts, e.g., Pt/ Al_2O_3 are used in a process to produce C_6H_6 and town gas from a hydrocarbon feed.

Palladium-Lead Catalysts

CHAS PFIZER & CO. INC.

U.S. Patent 3,477,962

A Pb-Pd hydrogenation catalyst having enhanced selectivity is used to catalyse the hydrogenation of an acetylenic bond to an olefinic bond (only). It is produced by impregnating a support material with a Pd salt and a Pb salt to provide an atomic ratio of Pb to Pd of from 1:1-5:1, and subjecting the impregnated support material to a reducing step in which the product is a catalyst containing metallic Pd. The catalyst can be regenerated by intimately mixing it with $NaHCO_3 \cdot H_2O_2$ in aqueous solution.

HOMOGENEOUS CATALYSIS

Palladium Catalyst for the Dimerisation of Butadiene

JAPAN SYNTHETIC RUBBER CO. LTD

British Patent 1,178,812

The catalyst consists of a Pd-tertiary phosphine complex containing a dienophile as a ligand. The dienophile may be, e.g., maleic anhydride, benzoquinone, fumaric acid, etc.

Use of Noble-metal Salts

NATIONAL DISTILLERS & CHEMICAL CORP.

British Patent 1,179,373

Substituted aromatic derivatives (especially monochlorobenzene) are obtained by reacting an aromatic compound (e.g., C_6H_6) with a Group VIII noble metal salt, e.g., $PtCl_2$ or $PdCl_2$.

Hydrogenation Catalyst

UNILEVER LTD

British Patent 1,179,504

Unsaturated aliphatic compounds, especially fatty acids and their esters (e.g., soya-bean oil), can be selectively hydrogenated in the presence of a catalyst consisting of $SnCl_2$ together with H_2PtCl_6 , H_2PtCl_4 or their alkali metal or ammonium salts. See also 1,180,729 and 1,180,730.

Rhodium Catalyst for Adiponitrile Synthesis

E. I. DU PONT DE NEMOURS & CO.

British Patent 1,181,137

Adiponitrile is prepared by the hydrogenation of 1,4-dicyano-butenes in the presence of a Rh complex, e.g., tris(triphenylphosphine) rhodium chloride.

Oxidation Catalyst

HALCON INTERNATIONAL INC.

British Patent 1,183,226

Aromatic hydrocarbons are converted to carboxylic acids by reaction with CO and a metal salt oxidant, e.g., a salt of Ru, Rh, Pd, Os, Ir, Pt, especially $PdCl_2$.

Oxidation Catalysts

KNAPSACK A.G.

British Patent 1,184,320

Catalysts for the production of an unsaturated ester from an olefin, a carboxylic acid and molecular O_2 consist of a supported mixture of Pd acetate, an alkali metal acetate and one or more U compounds.

Platinum Complexes

RHONE-POULENC S.A.

British Patent 1,184,534

The preparation, and use as catalysts in the manufacture of organic polysiloxanes, of the platinum chloride complexes $PtCl_2 \cdot 2P(NR^3)_3$, is described. Examples are $PtCl_2 \cdot 2P(NMe)_3$ and $PtCl_2 \cdot 2P(NEt)_3$.

Catalyst for Crystalline Allene Polymers

JAPAN SYNTHETIC RUBBER CO. LTD

British Patent 1,184,751

The catalyst is at least one compound of the formula $[\text{Rh X(L)}_2]_2$, (X is halogen, L is CO or C_2H_4).

Catalyst

IMPERIAL CHEMICAL INDUSTRIES LTD

British Patent 1,188,212

F-containing silanes and siloxanes are obtained by reacting a silane with an N-alkenyl amide of a perfluoralkyl carboxylic acid in the presence of supported Pt; H_2PtCl_6 ; complexes of Pt halides with olefines, complexes of H_2PtCl_6 with alcohols, aldehydes or ethers, or Rh chloride-phosphine complexes.

Catalytic Oxidations with Ruthenium

CELANESE CORP.

U.S. Patent 3,479,403

The activity of Ru as an oxidation catalyst is enhanced by maintaining the oxidation potential of the Ru at less than the oxidising potential of Ru(VIII) but greater than that of Ru(IV).

Homogeneous Hydrogenation of Olefins

JOHNSON MATTHEY & CO. LTD

Belgian Patent 725,915

A bis- or tris(triphenylphosphine)chlororhodium complex is used as a catalyst for the hydrogenation, hydroformylation or carbonylation of unsaturated compounds such as olefins, ketones etc.

FUEL CELLS

Hydrogen-permeable Membrane

ATLANTIC RICHFIELD CO.

British Patent 1,179,033

A fuel cell is operated by passing a mixture of a hydrocarbon and steam over a reforming catalyst and passing the hydrogen so formed through a permeable membrane into an electrolyte for electrochemical reaction. The membrane is of Pd or a Pd alloy, e.g., one containing 25% Ag.

Electrodes for Electrochemical Cells

LEESONA CORP.

British Patent 1,187,282

Such electrodes, e.g., for fuel cell anodes, consist of a Pd-Au alloy containing 34 to 64 at.% of Au.

CHEMICAL TECHNOLOGY

Removing Hydrogen from Liquid Metals

E. F. HILL

British Patent 1,178,281

The H_2 is allowed to diffuse from the liquid metal at 260 to 760° through a H_2 -permeable bimetallic barrier consisting of (a) a layer of Fe, Ni, Ta or Nb or their alloys (b) a layer of Pd, Pt or their alloys which is in contact with an oxidising atmosphere so that the H_2 is converted to water.

ELECTRICAL AND ELECTRONIC ENGINEERING

Electrically Heatable Filaments

NATIONAL RESEARCH & DEVELOPMENT CORP.

British Patent 1,184,184

A refractory-supported Pt filament is protected by a gas-impermeable glass layer having a softening point below 1500°C.

Bonding of Metals

PHILIPS ELECTRONIC & ASSOCIATED INDUSTRIES LTD

British Patent 1,184,701

An Al surface is bonded to a second metal surface by sputtering a layer of Ta, Ti or Nb on to the Al, depositing thereon a layer of Pt, a layer of Au, and bonding to the second surface with a soft solder of 95 wt% Sn and 5 wt% Ag.

Printed Circuits

PHOTOCIRCUITS CORP.

British Patent 1,186,558

A metal pattern (e.g., of Cu, followed Au or Ag) is deposited on to a catalytic insulating substrate. The substrate is catalytic throughout its interior for the electroless deposition of metal. The catalytic activity is provided by preliminary immersion of the substrate in PdCl_2 solution, for example, and then drying.

Capacitors

E. I. DU PONT DE NEMOURS & CO.

British Patent 1,187,360

Electrodes for capacitors consist of an alloy of at least three of the metals; Ru, Os, Rh, Pd, Pt, Ir, Ag, Au and Hg. An example contains 40-60 wt% Pt, 20-40 wt% Pd, and 20-40 wt% Au.

Cermet Resistors

BECKMAN INSTRUMENTS INC.

British Patent 1,188,346

A cermet resistance composition suitable for firing on to a non-conductive substrate to form a thin resistance layer of high power stability, consists of a mixture of finely ground particles of glass, a filler and an alloy of Ir, Ru, or Rh with Ir, Ru, Rh, Au, Ag, Pd or Pt.

Cermet Resistance Element

BECKMAN INSTRUMENTS INC.

U.S. Patent 3,479,216

A cermet resistance element is formed of a non-conductive base number having deposited thereon a single layer of resistance material formed of 50 to 95% of solidified glass and 5 to 50% of a conductive constituent. The conductive constituent consists of Ir and at least one of Pt, Ag, Ru, Rh and Pd, in finely divided particulate form and uniformly dispersed in electrically conductive relationship throughout the solidified glass.