

Bimetallic Catalysts from Pseudotetrahedral Iridium-Tungsten Clusters. Syntheses and Crystal Structures of $(\eta^5\text{-C}_5\text{H}_5)\text{WIr}_3(\text{CO})_{11}$ and $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2\text{Ir}_2(\text{CO})_{10}$

J. R. SHAPLEY, S. J. HARDWICK, D. S. FOOST, G. D. STUCKY, M. R. CHURCHILL, C. BUENO and J. P. HUTCHINSON, *J. Am. Chem. Soc.*, 1981, **103**, (24), 7383-7385

Convenient syntheses and molecular structures of two tetranuclear Ir-W clusters $\text{CpWIr}_3(\text{CO})_{11}$ (1) and $\text{Cp}_2\text{W}_2\text{Ir}_2(\text{CO})_{12}$ (2) ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) and their use as precursors to Al_2O_3 -supported bimetallic catalysts are reported during hydrogenolysis of n-butene. The $[\text{Ir}_4]$ catalyst had high selectivity for scission of the central C-C bond in butane, forming two molecules of ethane. The $[\text{WIr}_3]$ and $[\text{W}_2 + \text{Ir}_2]$ catalysts showed ethane selectivity of 70% or greater, but the $[\text{W}_2\text{Ir}_2]$ catalyst had < 50% ethane in the product stream.

Carboxylic Acids from Syngas

J. F. KNIFTON, *Hydrocarbon Process.*, 1981, **60**, (12), 113-117

A new route for preparing short-chain aliphatic carboxylic acids using homogeneous Ru and Rh catalysts, where the products may be based optionally upon syngas feedstocks alone, is described. Lower molecular weight carboxylic acids are homologised by synthesis gas in the presence of a solubilised Ru or Rh species plus a suitable I-containing promoter. Catalysts such as RuO_2 , $\text{H}_4\text{Rh}_4(\text{CO})_{12}$, $\text{Ru}_3(\text{CO})_{12}$, $\text{Ru}(\text{acac})_3$, RuCl_3 , $\text{RuCl}_2(\text{PPh}_3)_3$, $\text{Rh}(\text{acac})_3$, Rh_2O_3 , RhCl_3 , $\text{Pd}(\text{OAc})_2\text{-8PPh}_3$ are used. Catalyst selection, operating conditions, the homologation reaction, process description, and costs are described.

Ru-Catalyzed Oxidation of Acetylene to α -Diketones with Iodosylbenzene

P. MÜLLER and J. GODOY, *Helv. Chim. Acta.*, 1981, **64**, (8), 2531-2533

Disubstituted acetylenes are oxidised with PhIO in the presence of $\text{RuCl}_2(\text{PPh}_3)_3$ to give α -diketones in 65-85% yield. Under the same conditions terminal acetylenes are cleaved to carboxylic acids.

NEW PATENTS

METALS AND ALLOYS

Dispersion Strengthened Precious Metal Alloys

OWENS-CORNING FIBERGLASS CORP.

British App. 2,075,552/3 A

Alloys with superior creep resistance are obtained by the mechanical introduction of the oxide material, such as Y for Pt or Pt alloys. The thermomechanical processing of the products is described.

ELECTRICAL AND ELECTRONIC ENGINEERING

Pd-Thin-SiO₂-Si Diode. I. Isothermal Variation of H₂-Induced Interfacial Trapping States. II. Theoretical Modelling and the H₂ Response

B. KERAMATI and J. N. ZEMEL, *J. Appl. Phys.*, 1982, **53**, (2), 1091-1099, 1100-1109

The current-voltage characteristic and the small-signal frequency dependent admittance response of a Pd-thin-SiO₂-Si diode were measured. A method was developed to calculate the d.c. response and the small signal admittance of a MIS diode under a given applied voltage. The generated interfacial trapping states were responsible for the induced electrical changes in the Pd-thin-SiO₂-Si diodes.

Anodic Evolution of Oxygen on Sputtered Iridium Oxide Films

S. HACKWOOD, L. M. SCHIAVONE, W. C. DAUTREMONT-SMITH and G. BENI, *J. Electrochem. Soc.*, 1981, **128**, (12), 2569-2573

The catalytic properties of sputtered Ir oxide films (SIROF'S) in acidic electrolytes were studied. Long term stability is demonstrated. Typical steady state currents are 75mA/cm² at 1.85V, which is 50% higher than previously reported. The high current density and absence of corrosion demonstrate the superior catalytic properties of SIROF's vs. Ir over the entire voltage range studied.

MEDICAL USES

Carcinostatic Effect of a Caffeine-8-Ether-Platinum Complex

H. KRÖGER and J. KLOSA, *Naturwissenschaften*, 1981, **68**, (12), 628

The caffeine-8-ether-Pt complex (Cofplatin) was synthesised and given to rats and mice with various sarcomas, when cessation in growth in the tumours was seen. Cofplatin is a stable non-aggressive substance and further research is being done.

Dispersion-Hardened Metal Alloys

KERNFORSCHUNGSZENTRUM KARLSRUHE G.m.b.H.

European Appl. 44,351

An alloy composition hardened by dispersed carbide particles is formed by decomposing a ternary or higher mixed carbide in a suitable matrix alloy. The carbides are derived from Group IVB, VB and VIB transition metals while the matrix is a solid alloy of Group IVB, VB and VIB metals with Re or one of the platinum group metals.

CHEMICAL COMPOUNDS

Palladium Organotellurium Complexes

EASTMAN KODAK CO.

U.S. Patent 4,287,354

New photosensitive complexes for photographic elements are obtained from Pd chloride and new organotellurium compounds, $\text{Te}[(\text{CH}_2)_n\text{SiR}_3]_2$, where n is 1-10 and R is an alkyl, alkenyl or heterocyclic group.

ELECTROCHEMISTRY

Gas Separation Apparatus

A. P. SANDERS

British Appl. 2,078,539 A

A diffusion apparatus for selectively separating H_2 from other gases consists of a refractory base having an indented maze-like flow path which is coated with a H_2 permeable membrane of 90% Pd-10% Ag alloy. Several diffusion plates may be stacked to form a diffusion unit for a thermal water dissociation apparatus.

Catalytic Electrode

WESTINGHOUSE ELECTRIC CORP.

European Appl. 40,897

An electrode for use in the oxidation of SO_2 , as part of a process for the large-scale production of H_2 , is obtained by impregnating a porous substrate, such as C with a salt of a platinum group metal, preferably Pd, in a specified manner.

Electrode for Use in Brine Cells

ORONZIO DE NORA IMPIANTI ELETTROCHIMICI S.p.A.

U.S. Patent 4,287,032

An improved membrane electrode is formed from a powdered electroconductive, electrocatalytic material, such as a mixture of Ru, Ir and Ti oxides, bound together with a fluorolefin polymer having a hydrophilic surface. The hydrophilic surface may be obtained by exposing a PTFE polymer to ionising radiation from Co^{60} in the presence of hydrophilic group precursors.

ELECTRODEPOSITION AND SURFACE COATINGS

Method of Electroplating Platinum-Rhodium Alloys

U.S. SECRETARY OF THE INTERIOR

U.S. Patent 4,285,784

In a method for obtaining a Pt-Rh coating of predetermined composition and thickness, in which the composition of the alloy is uniform throughout the coating, individual Pt and Rh baths are prepared by dissolving an anode of the appropriate metal in a molten cyanide salt bath, and a mixed bath is then formed containing the required proportion of each metal. Alloys may then be plated from the mixed bath using alternating Pt and Rh anodes.

Palladium Plating

DEGUSSA A.G.

German Offen. 3,013,029

Bright flawless Pd deposits are obtained from an electroplating bath at pH 6-8 containing, per litre, 1-15g of Pd in the form of a Pd diaminodinitrile, 10-15g NH_4NO_3 , 0.05-1g of a water-soluble benzophenone derivative such as benzophenone sulphonic acid, and optionally 1-20g of a complexing agent such as EDTA.

LABORATORY APPARATUS AND TECHNIQUE

Solid Electrolyte Gas Sensor

SYBRON CORP.

British Patents 1,604,445/6

A concentration O_2 cell is in the form of a tube divided at its centre point with a disc of ZrO_2 or other solid electrolyte material. Pt heater wires embedded in the wall of the tube maintain equal temperatures at both sides of the sensor disc and the temperature of the two gas chambers is monitored by thermocouples, such as Pt or Pt-Rh, inserted in the tube close to the sensor disc.

Oxygen Sensor for Combustible Gases

WESTINGHOUSE ELECTRIC CORP.

U.S. Patent 4,285,790

A molten carbonate electrochemical cell is used to remove O_2 in combination with CO_2 from an O_2 -combustible gas mixture, at low temperature (400-700°C), in order to provide measurement of the O_2 content of the gas via a Pt electrode solid electrolyte O_2 sensor.

Solid Pole Oxygen Sensor

TOYOTA JIDOSHA KOGYO K.K.

U.S. Patent 4,292,157

A simplified O_2 sensor for automotive use is produced by burying one end of a Pt or Pt-Rh lead in a single pole of Co/CoO, for example, coating the pole with a conductive Pt paste and then encapsulating the pole in a solid electrolyte, preferably Y-stabilised ZrO_2 which is dried and pressure-moulded into a pellet. The surface of the pellet is then plated or baked to form a second Pt electrode.

JOINING

Method of Welding Precious Metal Foils

T. KIYOSUMI

U.S. Patent 4,291,216

A method involving seam welding of a sandwich layer of metals enables a corrosion-resistant substrate to be coated with a protective layer of precious metal. In the method, which may be used to produce electrodes, a Ti or another valve metal substrate is covered by a thin ($\sim 10\mu\text{m}$) layer of Pt, and then with a thicker layer of stainless steel or another corrosion resistant metal and after seam welding of the sandwich the outer metal layer is removed by etching with aqua regia.

HETEROGENEOUS CATALYSIS

Metal Supported Catalysts for Methanation

JOHNSON MATTHEY & CO. LTD.

British Patent 1,603,101

Synthesis gases are reacted in a temperature stable reactor having metallic channels made from or bearing a catalytic material which catalyses the methanation reaction. The preferred catalysts are alloys of Ni, Re or the platinum group metals, Ru alloys or platinum group metal impregnated Ni or Cr base metal alloys having refractory metal oxide washcoats.

Activating Catalyst Supports

GALLAHER LTD.

British Patent 1,604,081

Conventional pelleted Al_2O_3 and zeolite catalytic pellets are activated by providing a surface deficiency of hydroxyl groups just before impregnation with the catalytic metal, such as Pt and Pd. The hydroxyl deficiency may be obtained by heating the support material, by crushing the particles or by providing Lewis acid sites. Such catalysts may be used in smoking materials or for exhaust gas purification.

A Process for the Preparation of Hydrocarbons

SHELL INTERNATIONALE RESEARCH MIJ.B.V.

British Appl. 2,077,754 A

Syngas with a H_2 : CO molar ratio less than 1 is contacted in a first stage with a Fe-containing catalyst having Fischer-Tropsch as well as CO-shift activity. A H_2 /CO mixture optionally separated from the first stage product and having a H_2 : CO molar ratio of at least 1.5 is contacted in a second stage with a Co- or Ru-containing Fischer-Tropsch catalyst. In this way the stability of the process is improved.

Production of Alcohols from Synthesis Gas

BRITISH PETROLEUM CO. LTD.

British Appl. 2,078,745 A

A supported Rh-Re catalyst, optionally containing Fe, Mn, Mo, W, Ru, Cr, Zr, U and/or Th, is used for the commercial scale production of methanol-ethanol mixtures from synthesis gas.

Catalytic Converter

MINNESOTA MINING & MANUFACTURING CO.

European Appl. 40,235

In a converter of specified design for decomposing ozone in aircraft atmospheres, the active catalyst may be Pt, Pd or Ni.

Hydrocracked Lubricating Oils

MOBIL OIL CORP.

European Appls. 42,238/9

Low pour point oils are obtained by hydrocracking, catalytic dewaxing and hydrotreating a suitable feedstock. Pd and Pt catalysts may be used in some stages of the process.

Water Dissociation

HORIZON MANUFACTURING CO. *U.S. Patent 4,287,169*

The water is reacted with an amalgam of Hg, Na and Al to form the hydroxide $\text{Na}_2\text{Al}(\text{OH})_6$ which is then decomposed in the presence of a catalyst containing a platinum group metal, preferably Rh; Ge, Sb, Ga, Th, In, Cd, Bi, Pb, Zn and/or Sn, and optionally Au.

Catalytic Heat Exchange Apparatus

JOHNSON MATTHEY INC.

U.S. Patent 4,288,346

A gaseous combustion mixture flows over the surface of a metal/ceramic screen consisting of Al_2O_3 carrying, on one side, a catalytic coating of one or more platinum group metals. Heat produced by the catalytic combustion is rapidly transferred to a gas stream flowing across the other face of the Al_2O_3 screen. The claims specifically refer to use of an Al_2O_3 cement derived from an aqueous dispersion of Al metal powder, Cr salt and an Al phosphate binder.

Polymetallic Reforming Catalyst

MOBIL OIL CORP.

U.S. Patent 4,288,348

More severe reforming conditions may be used in the reforming of naphtha fractions when the catalyst consists of Re, separate particles of Pt-Re/ Al_2O_3 and Ir/ Al_2O_3 .

Promoted Palladium Catalysts for Methanol Synthesis

UNION CARBIDE CORP.

U.S. Patents 4,289,709/10

Pd containing Li, Sr, Ba and/or Mo promoters is selective towards the production of methanol from synthesis gas at a temperature 200–400°C and a pressure 150–20,000 psia. In *U.S. Patent 4,289,710* the Pd catalyst is promoted by 0.5–1.0% Ca.

Oxidation of Methane

JOHNSON MATTHEY & CO. LTD. *U.S. Patent 4,289,737*

A catalyst which will oxidise organic contaminants, such as CH_4 , present in exhaust gases, at low temperature, consists of a honeycomb support bearing a high surface area metal oxide layer containing Group II, III and IV metal oxides and a second active layer containing 35% Rh and 65% Pt. The catalyst operates between 300–325°C.

Multimetallic Reforming Catalyst

EXXON RESEARCH & ENGINEERING CO.

U.S. Patent 4,292,204

A small amount of Ir (0.01–0.2%) is added to a hydrogenation-dehydrogenation catalyst containing 0.1–2% Pd and 0.1–2% Re to increase the aromatic content of the reformat and to reduce the coking tendency of the catalyst.

Urethane Catalyst

BAYER A.G.

German Offen. 3,009,489

The formation of aromatic urethanes from the corresponding nitro compounds, CO and alcohols is catalysed by Pd chloride in the presence of a co-catalyst mixture containing Fe powder.

Oxidation Catalyst

HOECHST A.G.

German Offen. 3,010,950

A catalyst for the oxidation of flue gases or I.C.E. exhaust gases consists of an Al-Cr steel carrier, surface-oxidised in air at elevated temperature, coated with Ce dioxide, and impregnated with Pd and Pt.

HOMOGENEOUS CATALYSIS

Synthesis of Unsaturated Esters and Lactone

MONTEDISON S.p.A.

British Patent 2,003,875 B

Carboxylation of butadiene in the presence of a phosphoric complex of Pd, such as $\text{Pd}(\text{PPh}_3)_2$, produces unsaturated esters and lactone.

Preparation of Aliphatic Carboxylic Acids

TEXACO DEVELOPMENT CORP.

British Appls. 2,078,722/3 A

Rh compound and complex catalysts, such as Rh oxide, acetylacetonate and carbonyls, are used together with an iodide or bromide promoter for the synthesis gas homologation of acetic acid and other aliphatic carboxylic acids. In *British Appl.* 2,078,723 A similarly promoted Pd and Ni catalysts, such as Pd acetate and acetylacetonate, are used in the same process.

Ruthenium Carboxylate Catalyst for Ethylene Glycol Production

HALCON RESEARCH & DEVELOPMENT CORP.

British Appl. 2,079,278 A

Homogeneous triarylphosphine Ru carboxylate catalysts produce high yields of ethylene glycol by the hydrogenation of glycoaldehyde, under moderate reaction conditions, without significant acetal formation.

Heteronuclear-Bridged Rhodium Cluster Hydroformylation Catalysts

UNION CARBIDE CORP.

U.S. Patent 4,288,380

Robust catalysts, better able to meet the severe conditions encountered in low-pressure oxo hydroformylation reactions, are clusters of formula $\text{Rh}(\text{MR})_m(\text{CO})_p(\text{M}'\text{R}')_q$ where M, M' are Group VA metals, R, R' are monovalent organic radicals and m, p and q are 2-6. The preferred catalyst is $\text{Rh}_3(\text{PPh}_2)(\text{CO})_3(\text{PPh}_3)_2$.

Rhodium Salt-Magnesium Catalyst for Synthesis Gas Conversion

HOECHST A.G.

U.S. Patent 4,288,558

Acetic acid, ethanol, acetaldehyde, etc., may be produced from synthesis gas by using a highly selective catalyst containing Rh salts or complexes, having a valency below 3, together with Mg salts or complexes. Suitable catalysts contain either $\text{Mg}_3[\text{RhCl}_6]_2$ or $\text{Mg}[\text{Rh}(\text{CO})_2\text{Cl}_2]_2$.

Palladium Hydrogenation Catalysts

INSTITUT NEFTEKHIMICHESKOGO SINTEZA IM. A.V. TOPCHIEVA AN. SSSR

Russian Patent 725,375

The selective hydrogenation of dienes or acetylenes to olefins is catalysed by a complex of a Pd salt with butylamine, octylamine, 4-amythiacyclohexane, 3-methyl-thiophane, dibutylsulphide, 9-12C alkylsulphoxides, cetyl alcohol or polyethylene glycol reduced with diisobutyl Al hydride.

FUEL CELLS

Noble Metal-Chromium Alloy Catalysts

UNITED TECHNOLOGIES CORP.

British Appl. 2,078,254 A

An electrocatalyst, particularly for acid fuel cells, with twice the activity of an unalloyed noble metal consists of an alloy of Pt or another noble metal with Cr, preferably 25 at.%Cr. The catalysts may be used in exhaust gas purification and chemical reactions.

CHEMICAL TECHNOLOGY

Uptake of Platinum Group Metals by Plants

JOHNSON MATTHEY & CO. LTD.

British Patent 1,604,768

Precious metals may be recovered from waste mineral ores by growing green-leaved plants on the ore and then recovering the metals, by dehydration and carbonisation, from the harvested plants. The treated ore is preferably spread over fertile land or it may be used in the form of an aqueous reservoir containing the discharged ore.

Solvent Extraction Recovery of Ruthenium

COMMISSARIAT A L'ENERGIE ATOMIQUE

U.S. Patent 4,282,112

Radioactive Ru in HNO_3 nuclear waste solutions is recovered by contact with an organic phase consisting of an organophosphorus compound having electron donor S atoms, especially di(2-ethyl-hexyl)-dithiophosphoric acid, in the presence of a compound, such as sulphonic acid, which will displace NO ions of the Ru complex present in HNO_3 .

Promoted Amine Extraction of Platinum Group Metals

MATTHEY RUSTENBURG REFINERS

French Appl. 2,472,025

In a method of separating Pt, Ir and/or Pd from a solution containing base and other platinum group metals, the solution is adjusted to a pH below 7 and then contacted with an organic phase containing amines or quaternary ammonium compounds and alcohols, phenols and/or carboxylic acids. Pt, Ir and/or Pd are extracted into the organic phase from which they may be separated by means of an acid.

GLASS TECHNOLOGY

Photochromic Glass for Lenses

CORNING GLASS WORKS *European Appl. 41,789*

Spectacle lenses for persons suffering from pigment deficiency eye diseases are made from a glass having an integral coloured surface layer and zero transmission of short wavelength radiation photochromically activated by Ag, which may contain 1–50 ppm of Pd and/or Au and up to 5% of lanthanide metal colorants.

ELECTRICAL AND ELECTRONIC ENGINEERING

Low Resistivity Composite Conductor

STANDARD MICROSYSTEMS CORP.
British Appl. 2,077,993 A

The gate electrode of a MOS device has a layer of a highly conductive material between two layers of polysilicon. This provides a gate electrode of reduced sheet resistivity. The highly conductive layer must be a metal silicide formed by depositing a layer of metal, such as Pt, and heating to form the silicide; or the metal silicide may be deposited directly.

High Pressure Metal Vapour Discharge Lamp

TOKYO SHIBAURA DENKI K.K.
British Appl. 2,080,019 A

Stable discharge lamps are obtained by including in the sealed arc tube a radioactive material having a half-life less than 1×10^4 years. Suitable radioactive materials including ^{106}Ru , ^{110}Ag , ^{144}Ce , ^{194}Au and various lanthanide metal isotopes, may be impregnated onto In and La metal substrates.

Optical Recording Element

EASTMAN KODAK CO. *European Appl. 42,307*

The element has a heat deformable layer, which may be made from vacuum-evaporated Rh or Pt, on which is deposited a barrier layer of a suitable polymer.

Capacitor Element

FUJITSU LTD. *European Appl. 44,742*

Au-Pd-Au/Si electrode plates may be used on capacitor dielectrics and sourced by conduction wires of specified length (based on signal wavelength) which may be made of Au.

High-Resolution Mask for Magnetic Bubble Domain Structures

ROCKWELL INTERNATIONAL CORP.
U.S. Patent 4,284,678

The mask consists of a thin (0.2–2 μm) layer of X-ray or low voltage E-beam transparent material (such as parylene) selectively coated with an opaque metal layer of Pt, Ir, Au, U or a lanthanide metal oxide.

Dual Schottky Contact Avalanche Semiconductor Structure

THOMSON-C.S.F. *U.S. Patent 4,286,276*

The structure has two conventional electrodes interdigitated with a supplementary electrode and separated by intervals of the same order of magnitude as the thickness of the active layer. The Schottky contact used is made of Pt.

TEMPERATURE MEASUREMENT

Heat Flow Measurement System

ELCON RESEARCH LTD. *British Appl. 2,077,435 A*

Thick film Pt resistance thermometers are used in a system which measures the heat flow in a subsystem of a central heating system.

Resistance Thermometer

HAYASHI DENKO K.K. *British Appl. 2,079,533 A*

A Pt resistance wire is secured in bores in a ceramic insulating system by means of a filling of ceramic particles between 30 and 150 μm in diameter. Use of particles rather than crushed insulator materials facilitates the filling operation and ensures that the spaces between the coils are fully filled.

MEDICAL USES

Silver-Tin-Copper-Palladium Dental Alloy

SPECIAL METALS CORP. *British Appl. 2,076,854 A*

Dental amalgam compositions which eliminate the formation of corrosive Sn-Mg phases, contain an alloy of 30–70% Ag, 15–37% Sn, 0.05–0.95% Pd, up to 4% Zn, up to 6% In, up to 2% Cd, up to 2% Al, up to 5% Ga, up to 2% Ru, up to 3% Hg and a balance of Cu. The alloy is amalgamated with 30–56% Hg.

Platinum Anti-Tumour Complexes

KUREHA KAGAKU KOGYO K.K. *European Appl. 41,792*

Pt complexes have a glycine dimer ligand and one or two carboxyl groups which are converted into ester or salt form to increase their water solubility and to decrease side-effects in use.

Cardiac Stimulator

SORIN BIOMEDICA S.P.A. *European Appl. 43,461*

The contact tip of a cardiac electrode is of Pt-Ir alloy coated with Pt sponge. The coating is obtained electrolytically and the porous structure is consolidated by sintering.

Dental Alloy

DEGUSSA A.G. *German Offen. 3,009,650*

A Au-free dental alloy is based on Pd, Cr and Co and may contain, 25–35% Pd, 5–15% Cr, 5–15% Mo and/or W, 2–6% Ce, 0.2–0.8% B, remainder Co.