

Ethylene Dimerisation in the Presence of Rhodium Complex with Tin Chloride Ligands

V. M. IGHATOV, N. V. BORUNOVA, C.-I. DZEN, A. F. LUNIN and L. KH. FREIDLIN, *Neftekhimiya*, 1982, **22**, (6), 749-753

Studies of the catalytic properties of Rh complexes with SnCl_3 -ligands, $[\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4]^{4+}$, were made during ethylene dimerisation. The catalyst was more active and stable than $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$. The most active complex had a ratio Sn:Rh=2 and concentration of HCl > 0.5 mole/l. Ethylene dimerisation reaction was first order for the catalyst and ethylene, and was highly selective, forming an equilibrium mixture of butene: butene-1(3%) and butene-2(97%).

FUEL CELLS

Oxidation of H_2 at Gas Diffusion Electrodes in H_2SO_4 and HBr

G. G. BARNA, S. N. FRANK and T. H. TEHERANI, *J. Electrochem. Soc.*, 1982, **129**, (11), 2464-2468

The oxidation of H_2 at a Pt-black catalysed gas diffusion fuel cell electrode was found to be diffusion limited in H_2SO_4 , but kinetically controlled in 48% HBr. The method to activate the anodes completely wets all the Pt in the anode. All of this wetted Pt then participates in the oxidation of H_2 . This proves that the anodes are flooded and are operating at the theoretical current limit. Further improvements will be achieved through using Pt/C where the available surface area of Pt is maximised.

NEW PATENTS

METALS AND ALLOYS

High Chromium Superalloy

JOHNSON MATTHEY P.L.C. *European Appl.* 65,812
Alloys having good high temperature 1000-1100°C resistance to molten glass and good mechanical properties, for use in centrifugal spinners for glass fibre production, are Ni-Cr alloys having less than 25 vol.% of γ' precipitate and containing up to 1.7% C, 0.3-4% Pt and/or Ru and up to 1.5% Ti and/or Al.

ELECTROCHEMISTRY

Electrochemical Cell

THE ELECTRICITY COUNCIL *British Appl.* 2,098,238 A
The efficiency of an electrochemical cell having RuO_2 , Pt-Ir or platinised Ti electrodes is improved by positioning a turbulence promotor, such as a plastic mesh insert, in a flow path over one of the cell electrodes. The cell may be used for electrochemical reduction of oxidation.

ELECTRICAL AND ELECTRONIC ENGINEERING

Platinum Silicide Ohmic Contacts to Shallow Junctions in Silicon

S. S. COHEN, P. A. PIACENTE, G. GILDENBLAT and D. M. BROWN, *J. Appl. Phys.*, 1982, **53**, (12), 8856-8862

Ohmic contact to shallow pn^+ and pn^+ junctions in Si were studied. Thin layers ($\sim 200\text{\AA}$) of Pt were sputter deposited and reacted with the Si substrate at 590°C to give a stable Pt silicide. A four terminal Kelvin-resistor structure was used to measure accurately the contact resistance. Pre-deposition and in situ etching resulted in considerable improvement in the measured specific contact resistance. Values well within the range required were obtained.

An Evaluation of Palladium and Palladium-Silver Alloy in a Dual-in-Line Package Switch

W. R. HAIN, J. A. CLISURA and W. L. RUDLOFF, *IEEE Trans. Components, Hybrids, Manuf. Technol.*, 1982, **CHMT-5**, (1), 16-22

Pd and 60%Pd-40%Ag were evaluated as potential substitutes for Au contacts in a dual-in-line package switch, of the rocker type. Switches were evaluated for thickness and hardness, formability and adhesion, porosity before and after 2000 cycles, wearability and contact resistance before and after 2000 cycles. Results show that Au to Pd or Au to 60%Pd-40%Ag will provide stable contact resistance with acceptable wear properties.

Hydrogen Evolution Electrode

DIAMOND SHAMROCK CORP.

European Appl. 62,950/51

Cathodes for H_2 evolution from aqueous electrolytes consist of a valve metal support coated with a catalyst finely dispersed in a matrix of semiconducting polymer. The polymer may be polyphenylene and the catalyst is a platinum group metal.

Hydrogen by Electrolysis

WESTINGHOUSE ELECTRIC CORP.

European Appl. 63,420

An electrolyser for the production of H_2 from dilute H_2SO_4 saturated with SO_2 consists of a series of half cells in which the anodes are preferably pellets of activated vegetable C mixed with 1-5% Pt powder.

Improved Anode for Halogen Production

GENERAL ELECTRIC CO.

U.S. Patent 4,333,805

Cl_2 or another halogen is produced electrolytically in a cell having a new catalytic anode consisting of 90% Ru oxide and 10% Mn oxide.

Ruthenium-Bipyridine Complexes in Water Photolysis

RIKAGAKU KENKYUSHO *U.S. Patent 4,338,291*

Specified transition metal phthalocyanine complexes may be used to catalyse the production of H₂ from protons and viologen cation radicals formed by the photolysis of water containing a viologen, EDTA and a Ru(bipy)₃ complex.

Hydrogen Production

INSTITUTE OF GAS TECHNOLOGY

U.S. Patent 4,341,608

In a process for liberating H₂ by water electrolysis, the O₂ produced simultaneously is used to oxidise a biomass of lignins and/or monosaccharides. The electrodes may be Pt, Pt-W, Pt-Ta or a Raney alloy.

ELECTRODEPOSITION AND SURFACE COATINGS

Palladium Electrodeposition

HERAEUS QUARZSCHMELZE G.m.b.H.

U.S. Patent 4,339,311

Adherent, semiglossy to glossy, pore-free coatings are obtained by electrodeposition from Pd baths containing a specified amine but no NH₃. A typical bath contains per litre, 10g Pd as K₂[Pd(NO₂)₄], 60ml N-(2-aminoethyl)-1,3-diamino propane, 30g NaNO₃ and 5g K citrate.

Platinum-Containing MCrAlY Coatings for Superalloys

UNITED TECHNOLOGIES CORP. *U.S. Patent 4,346,137*

The addition of at least 13% of Pt and/or Rh to MCrAlY-type coating alloys brings the thermal expansion coefficient of the coatings closer to that of the superalloy substrate, and consequently improves the high temperature fatigue life of the coatings. The coating alloys, mainly for use on turbine blades, contain 8–30% Cr, 5–20% Al, 10–60% Ni, 8–30% Co, 0.005–1% of Y, Sc and/or La and a balance of Pt and/or Rh.

Rhodium Electroplating

DEGUSSA A.G. *German Offen. 3,100,997*

Fault-free bright Rh deposits of a white-gold colouration are obtained from baths containing Rh sulphate or phosphate, sulphuric and/or phosphoric acid and a sulphonic acid. A typical bath contains, per litre, 2g Rh as Rh sulphate, 40g H₂SO₄ and 0.5g of a 65% solution of phenolsulphonic acid.

Palladium-Nickel Electroplating

LANGBEIN-PFANHAUSER WERKE A.G.

German Offens. 3,108,466/67

The quality of coatings formed by electrodeposition from a bath containing (per litre) 5–30g Pd and 5–30g Ni (as respective ammine complexes) and a carrier electrolyte, is improved by including an acetylenic alcohol amine in the solution.

LABORATORY APPARATUS AND TECHNIQUE

Determination of Anaesthetic Gas in a Carrier

DRAGERWERK A.G. *British Appl. 2,098,741 A*

Au electrodes and a Pt wire catalytic heater are used on a phthalocyanine detector for determining the amount of anaesthetic gas being fed to a patient.

Sensor for Monitoring the Heating Value of Fuel Gases

WESTINGHOUSE ELECTRIC CORP.

British Appl. 2,099,589 A

A fuel gas is sampled and the sample mixed with excess O₂ and completely burned in a chamber, for example in the presence of a heated Pt sensing electrode which also acts as a catalyst. Either the O₂ consumed or remaining after combustion is used as a measure of the heating value of the fuel gas.

Infrared Radiation Detector

COMMONWEALTH OF AUSTRALIA

European Appl. 60,854

A detector has a substrate covered with a detector element formed by an ultrathin i.r. absorbing film of Pd, Pt, Ir or Ni less than 10nm thick or a Au film less than 20nm thick.

Gas Sensors

SIEMENS A.G.

U.S. Patent 4,338,281

Thin film semiconductor gas sensors of Pt oxide or Pd oxide, for CO or hydrocarbons are provided with an integrated heating element. The connecting wires may be of Pt, Au, Ni or Al.

HETEROGENEOUS CATALYSIS

Pt-Re Catalyst for Aromatic Hydrocarbon Production

EIF FRANCE

British Appl. 2,096,481 A

An improved catalyst for the dehydrocyclisation of paraffins, especially useful for the production of light aromatics, contains 0.1–1.5% Pt, 0.1–1.5% Re incorporated into the support in the form of a carbonyl sublimed or dissolved in acetone and a small amount of S introduced as a H reducible or decomposable S compound supported on a zeolitic aluminosilicate.

Catalytic Combustion Engines

RICARDO CONSULTING ENGINEERS P.L.C.

British Appl. 2,097,059 A

Each engine cylinder has a precombustion chamber communicating through a transfer passage to produce swirl around the chamber, and has a pair of parallel catalytic gauzes, for instance of Pt, mounted adjacent to both the mouth of the transfer passage and a fuel injector nozzle, so as to be clear of the swirl path of the gas circulating in the chamber. The

injector injects a fuel spray between the catalytic gauzes so as to brush each screen and impinge on a heater plug. The system is used in diesel engines.

Fischer-Tropsch Catalyst

RESEARCH ASSOCIATION FOR PETROLEUM ALTERNATIVES DEVELOPMENT *British Appl. 2,099,716 A*
A catalyst giving high CO conversion in the production of hydrocarbons from synthesis gas consists of an Fe-based Fischer-Tropsch catalyst, a zeolite and Ru, Rh, Pd, Ir, Co and/or Mo.

Fuel and Air Injectors for Use in Gas Turbine Engines

ROLLS-ROYCE LTD. *British Appl. 2,100,852 A*
A premixing system which thoroughly mixes fuel and air being injected into the combustion chamber of a gas turbine using catalytic ignition ensures lower pollution levels in the resulting exhaust gas. Catalytic ignition is carried out using Pt catalysts located in the combustion chamber.

Metal Fibre Catchment System

JOHNSON MATTHEY P.L.C. *European Appl. 63,450*
A getter pad for recovering Pt and Rh in nitric acid plants consists of an agglomeration of randomly orientated unwoven fibres of Ru, Pd, Ir, Pt, Au, Ag, Rh or an alloy of these metals. The pads, which are preferably of Pd or Au-Pd alloy, result in increased metal recovery and extended operating life over conventional woven getter pads.

Recombination Catalyst

VARTA BATTERIE A.G. *European Appl. 66,676*
H₂ and O₂ produced in batteries are recombined on a catalytic unit. The unit consists of a web of PTFE and active C impregnated with Pd powder and hydrophobed with a PTFE suspension.

Catalyst Packing Module

ATOMIC ENERGY OF CANADA LTD. *European Appl. 68,862*
A specified honeycomb catalyst packing module is designed to increase the vapour-liquid transfer rate in the isotopic exchange reaction between H₂ and H₂O. The active catalyst is a stainless steel gauze coated with a mixture of PTFE and platinised C powder.

Hydrocarbon Processing Catalyst

U.O.P. INC. *U.S. Patent 4,337,146*
The conversion of paraffins to aromatic hydrocarbons is catalysed by a mixture of 0.01–2% platinum group metal, 0.01–5% Re, 0.005–5% Fe and 0.1–3.5% Cl supported on a refractory oxide carrier, preferably Al₂O₃.

Catalyst Fabrication

JOHNSON MATTHEY INC. *U.S. Patent 4,340,505*
The amount of noble metal used in coating the exterior of a cylindrical catalytic device having a pre-

coated honeycomb interior is reduced by protecting the ends of the device with a reusable impermeable jacket fixed with a Velcro fastening.

Catalysts for Paraffin Dehydrogenation

U.O.P. INC. *U.S. Patent 4,341,664*
The dehydrogenation of paraffins to olefins is catalysed by a composition consisting of a carrier such as Al₂O₃ supporting 0.05–1% platinum group metal, 0.01–1% Ag, 0.05–1% Re (deposited from a carbonyl complex) and 0.25–3.5% Group IA or IIA metal.

Alkali-Doped Heterogeneous Group VIII Metal Catalysts

ALLIED CORP. *U.S. Patent 4,346,240*
A new class of heterogeneous catalysts, useful in the hydrogenation of carboxylic acid esters to primary alcohols, contains platinum group metals in combination with Group IA organic compounds on a C support. Typical catalysts are K naphthalene and Ru/C and K benzophenone and Rh/C.

Selective Hydrogenation of Hydrocarbon Fractions

INSTITUT FRANCAIS DU PETROLE *U.S. Patent 4,347,392*
A Pd catalyst, having Pd crystallites of average size of at least 50Å supported on Al₂O₃, is selective for hydrogenating impurities in an ethylene and/or propylene cut. A suitable catalyst may be obtained by calcining an impregnated support at relatively high temperature in air and then subjecting the calcined catalyst to reductive treatment with H₂.

Iridium-Ruthenium Catalyst for Hydrazine Decomposition

UNITED TECHNOLOGIES CORP. *U.S. Patent 4,348,303*
A multistart catalyst which will initiate the thermal decomposition of hydrazine-base monopropellants used in rocket motors, even after the initial fuel flow has been terminated and the decomposition temperature has fallen, has 0.5–8% of Ir and/or Ru deposited on a high area ceramic carrier. The precious metal composition, deposited on the carrier is used with other catalysts, such as Mo and Co.

Separately-Supported Polymetallic Reforming Catalyst

MOBIL OIL CORP. *U.S. Patent 4,349,433*
Improved conversion rates in naphtha reforming are obtained by using two separately supported catalyst components. The first catalyst contains 0.1–5% Pt and 0.1–5% Re on a refractory support and the second 0.1–5% Ir and 0.1–5% of a halogen component on another refractory support.

Photodecomposition Catalysts

CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE *French Appl. 2,493,181*
The photodecomposition of H₂O is catalysed by a platinum group metal or Re supported on Sr titanate.

HOMOGENEOUS CATALYSIS

Alcohol, Carboxylic Acid and Ester Production

UNIVERSITY OF SHEFFIELD *British Appl.* 2,101,128 A
An alcohol and a compound containing a carboxylate group are produced from aldehydes or an aldehyde and a ketone by disproportionation in the presence of a noble metal complex catalyst, such as $\text{Rh}_2(\text{C}_5\text{Me}_2)_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}$.

Organic Platinum Group Metal Catalysts

MINNESOTA MNG. & MFG. CO. *European Appl.* 61,241
New catalysts for hydrosilation reactions, especially for elastomer curing, contain Pt, Rh and Ir in a variety of complexes containing heterocyclic and especially phenazine molecules, such as (phenazine) $\text{PtCl}_2(\text{C}_5\text{H}_4)$, (imidazole) $\text{RhCl}(\text{CO})_2$ and (quinoxaline) $\text{RhCl}(\text{C}_8\text{H}_{12})$.

Very Large Transition Metal Clusters

WACKER-CHEMIE G.m.b.H. *European Appl.* 66,287
Highly active catalysts are clusters of formula $\text{M}_{55}\text{L}_{12}\text{X}_p$, where M is a Group I, V, VI, VII or VIII metal, L is an electron donor, X is halogen and p is 6–20. They may be produced from L_nMX_m ($n = 1-5$, $M = 1-6$) and an Al hydride or B hydride reducing agent. One complex is $\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6$ and similar Pt and Pd complexes are described.

Ruthenium Catalyst for Alcohol Production

UNION CARBIDE CORP. *European Appl.* 68,498
Methanol, ethanol and ethylene glycol are produced by the direct reaction of H_2 and CO in the presence of a Ru carbonyl complex catalyst characterised by three i.r. absorption bands. I_2 or an iodide must be present and the active catalyst is said to be a synergistic mixture of $\text{Ru}(\text{CO})_3\text{I}_3^-$ and $\text{HRu}_3(\text{CO})_{11}^-$.

Carboxylic Acid Homologation Catalyst

TEXACO INC. *U.S. Patent* 4,334,094
A system for catalysing the homologation of aliphatic carboxylic acids with synthesis gas contains Pd acetate, triphenylphosphine and CH_3I .

Rhodium Cluster Complex Catalyst

SNAMPROGETTI S.p.A. *U.S. Patent* 4,334,101
A hydroformylation catalyst is obtained by exchanging a zeolite with $[\text{Rh}(\text{NH}_3)_6]\text{Cl}_3$ and reacting the intermediate with H_2 and CO to form a trapped carbonyl cluster complex.

Catalyst for Ethanol Production

GULF RESEARCH AND DEVELOPMENT CO. *U.S. Patent* 4,346,020
A catalyst, effective for converting methanol, H_2 and CO to ethanol, consists of a Co carbonyl or hydrido component, a tertiary organic phosphine or arsine component, an I compound and a Ru compound, such as Ru acetylacetonate.

Doped Acetylene Polymer

JAPAN SYNTHETIC RUBBER CO. LTD.

U.S. Patent 4,349,664

Doped polymers having stable electrical properties are obtained by immersing an acetylene polymer in an organic solvent solution containing a dopant selected from platinum group metal complexes, carbonium salts, oxonium salts and parabenzoquinone derivatives. Typical dopants are $(\text{PhCN})_2\text{PdCl}_2$ and $(\text{COD})\text{PtCl}_3$. The polymers are used in solar cells.

FUEL CELLS

Electrode Catalyst for a Fuel Cell

HITACHI LTD. *British Appl.* 2,095,025 A

The use of a Pt-Ru heavy metal catalyst, such as Pt-Ru-Re and Pt-Ru-Sn, in acid electrolyte fuel cells which are driven by methanol, ethanol, etc., overcomes passivation problems experienced when Pt electrode catalysts are used.

Fuel Cell Construction

HITACHI LTD. *European Appl.* 60,560

A fuel cell has a pair of gas diffusion electrodes sandwiching a metal oxide matrix which retains the phosphoric acid electrolyte. The matrix may be made of zirconia, SiO_2 etc., and the gas diffusion electrodes of Pt/C powder.

Internal Reforming System for a Fuel Cell

ENERGY RESEARCH CORP. *European Appl.* 67,423

A catalyst for reforming the hydrocarbon fuel of a fuel cell is located either on or adjacent to a plate or diffusion membrane which produces a differential pressure within the cell. In one form a diffusion plate for the reformed gas is located downstream of the catalyst. This may be of a Ni-Pd alloy which is porous to H_2 gas.

Electrode System for Fuel and Electrolysis Cells

LICENTIA PATENT-VERWALTUNGS G.m.b.H.

U.S. Patent 4,344,832

The facing sides of two plate electrodes have parallel grooves which, when brought into contact with an intervening membrane, form gas channels. The surface of the plates may carry catalyst layers and a wicking arrangement. Ni fuel cell plates have a Pt-catalyst layer on the cathode side and a Pt-Pd-catalyst layer on the anode side.

GLASS TECHNOLOGY

Transparent-Opal Glass

CORNING GLASS WORKS *U.S. Patent* 4,336,303

In a process for obtaining colours in specified integral transparent-opal glass articles, a minute amount of a noble metal such as Pt, Rh, Ru, Au or Ag may be used as a coupling agent for TiO_2 .

ELECTRICAL AND ELECTRONIC ENGINEERING

Photoconductive Substrate

CANON K.K. *British Appls. 2,095,030/31 A*
Pt, Pd, Au and base metal may be used as a support layer for photoconductive amorphous Si material having varying O atoms. The photoconductive layer is mainly for use in solar cells.

Refractory Metal Layers on Ceramics

INTERNATIONAL BUSINESS MACHINES CORP. *European Appl. 61,010*
Conductive metal layers on ceramics which are free from glass are obtained by applying a refractory metal layer, such as a Mo paste, and then with a thin layer of Pd. On sintering the fusion of the refractory metal is catalysed by Pd and a compact layer is formed which excludes virtually any glass.

Resistive Pastes

N.V. PHILIPS' GLOEILAMPENFABRIEKEN *European Appl. 67,474*
A Ag-Pd resistive paste, which may be used in silk screening processes, contains an oxidic material based on Pd oxide together with a second oxide material to give improved temperature coefficients of resistivity. In preferred forms Ag-Pd alloy particles carry a coating of PdRhO₂ or an oxide having the formula Ag_xPd_{1-x}RhO₂ is incorporated in the resistor material.

Heterojunction Semiconductor Device

HITACHI LTD. *European Appl. 67,721*
A device is made from two layers of semiconductor, Si, one with impurity and the other without, whose interface forms the hetero junction. Pt may be deposited to form a Schottky gate, and Au employed in ohmic contacts.

Photoelectric Conversion Layer

HITACHI LTD. *European Appl. 67,722*
A H₂-containing amorphous Si layer is formed with specified temperatures in a plasma atmosphere. The layer may be improved by a semitransparent film of Pt, Pd or Au.

Magnetic Recording Medium

INTERNATIONAL BUSINESS MACHINES CORP. *European Appl. 68,131*
The medium is a sputtered polycrystalline film of composition Co_xPt_y where Co is 90 at.% or less of the material and Pt is 10-30 at.% of the material.

Gold Contact Surfaces

BELL TELEPHONE LABORATORIES INC. *U.S. Patent 4,337,133*
Durable, hard surfaces for electric contacts are made by sputtering Au together with a small amount of a refractory metal such as Ru, Os, Ir, Re or preferably Rh on to the contact surface.

Preparation of FETS

FUJITSU LTD. *U.S. Patent 4,343,657*
Pd₂Si and Pt₂Si₂ source and drain electrodes may be used on a FET device which is prepared by a method which includes direct selective nitridation followed by selective oxidation of the semiconductor substrate.

Platinum Cathode for a Gas Laser

FERRANTI LTD. *U.S. Patent 4,344,905*
Sputtering at the cathode electrode of a gas laser is considerably reduced if the cathode is made from a Pt pellet obtained by compressing Pt black powder under high pressure.

TEMPERATURE MEASUREMENT

Glass Coated Disc Thermistor

YELLOW SPRINGS INSTRUMENT CO. INC. *European Appl. 61,550*
A tri-metal contact film of Pt, Pd and Ag is metallurgically bonded to opposite surfaces of the resistance thermistor disc. This enables the assembly to be encased in a conformal glass coating after Ag-clad wires have been attached.

Thin Film Resistor

KABUSHIKI KAISHA KIRK *European Appl. 63,264*
In a Pt thin film resistance element for use in a temperature sensor or gas sensor, a thin metal film is formed on an insulating substrate, a kerf is formed in the film to increase its resistance, and a pair of lead wires are attached to the ends of the film. The film is Pt of thickness 0.01-0.1 μm.

MEDICAL USES

Gas Determination in Blood

HOFFMANN-LA ROCHE INC. *U.S. Patent 4,333,473*
The cutaneous blood gas concentration is measured by a microcathode while simultaneously the blood gas availability is measured by a large capacity cathode, the two heated cathodes forming a single unit. Both may be made of Pd and used with a single Ag anode.

Cis-Dichlorodiammine Platinum

MPD TECHNOLOGY CORP. *U.S. Patent 4,335,087*
Cis-Pt(NH₃)₂Cl₂ is obtained by adding solid KCl to an aqueous solution of [Pt(NH₃)₂(H₂O)₂] [NO₃]₂ at room temperature, heating to about 70°C and holding for about 1 hour, allowing to cool, with stirring, to room temperature and filtering immediately.

Dental Alloy

UNITEK CORP. *U.S. Patent 4,336,290*
A lower-cost dental alloy which does not discolour porcelain contains 80-90% Pd, 5-15% In, 1-5% Ga, 0.1-0.5% Al, 0.1-0.5% Si and 0.01-1% of Ru or Os.