

### Rhodium-Catalysed Low Pressure Hydroformylation of Higher $\alpha$ -Olefins: New, Thermally Stable Rhodium Catalysts by Reaction of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ with Phosphinous Acids

M. MATSUMOTO and M. TAMURA, *J. Mol. Catal.*, 1983, **19**, (3), 365-367

Rh-catalysed, low pressure hydroformylation of 1-dodecene was restudied in dodecylbenzene solution in the presence of a large excess of  $\text{PPh}_3$ . The formation of a new Rh complex,  $\text{Rh}_2(\text{CO})_2(\text{PPh}_3)_2(\text{R}_2\text{PO})_2$ , which is probably produced by reaction of  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$  with the phosphinous acid, improves the thermal stability of the Rh complex in the solution.

### Highly Reactive Rh(I) Hydrido Compounds

T. OKANO and T. YOSHIDA, *J. Synth. Org. Chem., Jpn.*, 1983, **41**, (4), 359-364

Three types of Rh(I) hydridotrialkylphosphine complexes, *trans*- $\text{RhH}(\text{N}_2)\text{L}_2$  ( $\text{L}=\text{P}(\text{t-Bu})_3$ ,  $\text{PPh}(\text{t-Bu})_2$ ,  $\text{PCy}_3$ ,  $\text{P}(\text{i-Pr})_3$ ),  $\text{Rh}_2\text{H}(\mu\text{-N}_2)\text{L}_4$  ( $\text{L}=\text{PCy}_3$ ,  $\text{P}(\text{i-Pr})_3$ ) and  $\text{RhHL}_n$  ( $n=3$ ,  $\text{L}=\text{P}(\text{i-Pr})_3$ ,  $\text{PEt}_3$ ;  $n=4$ ,  $\text{L}=\text{PEt}_3$ ) were prepared by reducing  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  with Na/Hg in THF. They proved to be extremely strong nucleophiles and were efficient catalysts for hydrogenation of nitriles, ketones and alkynes, and the H-D exchange reaction of  $\text{H}_2$  and H-C ( $\text{sp}^2$ ,  $\text{sp}^3$ ) bond with  $\text{D}_2\text{O}$  through activation of  $\text{H}_2$  and  $\text{H}_2\text{O}$ , respectively. They also catalysed the hydrogenation of carbonyl and nitro compounds with  $\text{H}_2\text{O}$ -CO and the hydroformylation of olefins with formaldehyde.

### Hydrogenation of Carbon Monoxide by Ruthenium Complexes with Iodide Promoters: Catalytic and Mechanistic Investigations

B. D. DOMBEK, *J. Organomet. Chem.*, 1983, **250**, (1), 467-487

CO and  $\text{H}_2$  are converted into organic products, including methanol, ethylene glycol and ethanol, by halide-promoted Ru catalysts in organic solvents. Iodide salts are exceptionally good promoters for this system. Two Ru complexes,  $\text{HRu}_3(\text{CO})_{11}^-$  and  $\text{Ru}(\text{CO})_3\text{I}_3^-$  are present during catalysis and essential for optimum activity.

### ELECTRICAL AND ELECTRONIC ENGINEERING

#### Pile Up of Implanted Phosphorus during Palladium Silicide Formation and the Characteristics of Schottky Barrier Diodes

A. KIKUCHI, *J. Appl. Phys.*, 1983, **54**, (7), 3998-4000  
Schottky barrier diodes, produced from  $\text{Pd}_2\text{Si}$  or Al-Si were fabricated on Si surfaces, whose impurity concentrations were controlled by P ion implantations. The forward voltages of Schottky barrier diodes made from  $\text{Pd}_2\text{Si}$  show a much greater lowering than those made from Al-Si for implanted doses of  $5 \times 10^{13}/\text{cm}^2$  and higher. Spreading resistance measurements show that the implanted P atoms are piled up at the  $\text{Pd}_2\text{Si}/\text{Si}$  interface during  $\text{Pd}_2\text{Si}$  formation, this reduces the effective barrier height.

## NEW PATENTS

### METALS AND ALLOYS

#### Brazing Alloy Containing Palladium

GENERAL ELECTRIC CO. *European Appl.* 76,991

An alloy for use in high temperature gas turbine engines contains 20-80% Pd, 2-13% Cr, 1-4% B, balance Ni, and is free from Si. Its brazing temperature is 982-1093°C. A preferred alloy contains 30% Pd, 10.5% Cr, 2.4% B and 57.1% Ni. The alloys have improved stress rupture properties, good ductility and oxidation resistance and are less expensive than Au alloys.

### ELECTROCHEMISTRY

#### Catalytic Electrode

DIAMOND SHAMROCK CORP. *European Appl.* 83,554

Catalytic electrodes for use in brine electrolysis are preferably made of valve metal coated with a mixture of 22-55 mol.% Ru oxide, 0.2-22 mol.% Pd oxide and 44-77.8% Ti oxide.

#### Water Photodecomposition Catalyst

SIBIT S.p.A.

*U.S. Patent* 4,370,263

An active catalyst for the photodecomposition of water either in the presence of or without a simplified redox system contains particles of Nb-doped  $\text{TiO}_2$  carrying a surface layer of Ru oxide. In an example, a catalyst obtained by adding Ru chloride to a filter cake of  $\text{Nb}_2\text{O}_5$  and  $\text{TiO}_2$  was used in the presence of a colloidal Pt water reducing catalyst and a Ru trisbipyridyl-methylviologen redox system.

### ELECTRODEPOSITION AND SURFACE COATINGS

#### Chemical Plating Activation

BAYER A.G.

*European Appl.* 81,129

Plastics and other substrates may be activated for subsequent chemical plating by the application of a Group IB or VIII metal organic compound where the organic portion contains one group to complex the

metal and at least one other functional group. A suitable compound is a Pd chloride complex of cyclohexene-1, 2-dicarboxylic anhydride or the corresponding AgNO<sub>3</sub> complex.

### Palladium Plating Bath

SIEMENS A.G. *European Appl.* 81,788

Uniform bright Pd films are obtained by electrodeposition from a bath made by adding 10–100ml phosphoric acid, density 1.71 to 600ml water at 60°C, neutralising to pH 6.5–8.5 with aqueous 25% ammonia, adding Pd chloride (5–40g as Pd), making up to 1 litre with distilled water and filtering.

### Palladium-Nickel Alloy Electrodeposition

LANGBEIN-PFANHAUSER WERKE A.G.

*German Offen.* 3,232,735

The corrosion resistance of electrolytically deposited Pd-Ni coatings is improved by adding benzene sulphonyl urea or an alkyl derivative of it to the plating bath. A preferred solution contains, per litre, 20g Pd as [Pd(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub>, 9g Ni as [Ni(NH<sub>3</sub>)<sub>6</sub>]SO<sub>4</sub>, 5g ammonium sulphate, 3g Na allyl sulphate, 0.5g phosphoric acid ester and 2g benzene sulphonyl urea.

## JOINING

### Low Temperature Integrated Circuit Die Attachment

FAIRCHILD CAMERA & INSTRUMENT CORP.

*European Appl.* 72,273

The die is attached to an underlying substrate by coating its back with Ag, coating the substrate with Au, Ag, Pt and/or Pd and joining the two surfaces with a Au-Sn, for example 80 : 20 solder alloy.

### Adherent Coatings

ADVANCED TECHNOLOGY INC. *European Appl.* 79,151

Ceramics are bonded to each other or to metals through a film or layer of a Sn alloy, for example with V or a carbide or carbonyl-former in an atmosphere of CO. The carbide- or carbonyl-former may be Rh, Ru, Os or Ir amongst others.

## HETEROGENEOUS CATALYSIS

### Olefin Hydroxylation

EXXON RESEARCH & ENGINEERING CO.

*European Appl.* 77,201

The hydroxylation of olefins with a gas containing O<sub>2</sub> and water to produce glycols is catalysed by an Os, Ru, Ir, Ti, Zr, Nb, Cr, Mo, W or Re oxide promoted with an Fe, Co, Ni, Cu, V, Cr, Mn, Sc, Ti, Mo, Ru, Rh, Pd or W halide, carboxylate, phenoxy, pseudohalide, mercaptan, sulphide, selenide or telluride, and a second promoter selected from Group IA, IIA or onium salts of the same anions. The preferred catalyst is OsO<sub>4</sub>, used with CuBr<sub>2</sub> and Et<sub>4</sub>NBr in producing propylene glycol.

## Food Treatment

JOHNSON MATTHEY & CO. LTD. *U.S. Patent* 4,364,727

The amount of pollutants present in a hot gas stream used for the heat treatment of food, for example in a baking oven, may be reduced by preheating an O<sub>2</sub>-containing stream with a pilot burner or electric heating element, mixing the O<sub>2</sub> stream with a second unheated O<sub>2</sub>-containing stream, injecting fuel into the O<sub>2</sub> streams and then passing the streams through a series of catalytic combustors of Pt, supported on a monolith coated with a refractory metal oxide. Using this system a turndown ratio of 15–20 : 1 is possible.

### Exhaust Purification Catalyst

K.K. TOYOTA CHIO KENKYOSHA *U.S. Patent* 4,367,162

A refractory oxide honeycomb carrying a first layer of ZrO<sub>2</sub> powder mixed with Al<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>-MgO<sub>2</sub> spinel and/or ceria powder and a catalyst layer of Ce oxide plus Pt and/or Pd is a highly efficient catalyst for I.C. engine exhaust purification. A typical catalyst composition contains 51.6% Ce oxide, 3% Pd and 0.5% Pt.

### Immobilised Platinum Metal Hydrogenation Catalysts

U.O.P. INC.

*U.S. Patent* 4,367,355

Group VIII metals, preferably Pt and Pd, are immobilised on an aminated polysaccharide, such as chitin or chitosan, in a highly dispersed state and form active catalysts in the hydrogenation of unsaturated compounds.

### Exhaust Purification Catalyst

TOYOTA JIDOSHA K.K. & CATALOR INDUSTRIAL CO. LTD.

*U.S. Patent* 4,369,132

A catalyst composition especially useful in automobile emission control applications, which remains active under low temperature conditions such as when the engine is idling, contains 0.0001–1 mole of Group IA metal oxide per kg catalyst and a Pt-Pd, Pt-Rh or Pt-Pd-Rh mixture containing at least 50% Pt supported on a cordierite, zircon, mullite, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, TiO<sub>2</sub>, MgO<sub>2</sub> or BaSO<sub>4</sub> carrier.

### Multimetallie Reforming Catalyst

EXXON RESEARCH & ENGINEERING CO.

*U.S. Patent* 4,370,224

Stable reforming catalysts which can operate with high efficiency under severe operating conditions contain 0.1–2% Pt, 0.1–2% Ir, 0.01–0.1% Cu, 0.001–3% Se and 0.1–2.5 of a halogen component on an inorganic oxide support.

### Preparation of Supported Platinum Metal Catalysts

W. R. GRACE & CO.

*U.S. Patent* 4,370,260

Exhaust purification catalysts having improved resistance to poisoning are obtained when a suitable inorganic oxide support is impregnated from a mixture containing a Pt sulphite complex, a Pd sulphite complex and Rh nitrate having a pH of 1–5.

### Fibre Packs for Ammonia Oxidation

JOHNSON MATTHEY & CO. LTD. *U.S. Patent 4,375,426*  
A catalyst assembly, especially for the oxidation of  $\text{NH}_3$  to nitric acid, includes an agglomeration of randomly oriented melt-extracted or melt-spun fibres of relatively short length, made from a platinum group metal or its alloy, supported on a metal gauze also preferably made from a platinum group metal or alloy. These catalyst assemblies give a performance at least as good as conventional gauzes and there is considerable metal saving.

### Halonitrobenzene Hydrogenation Catalyst (Phosphoric Acid Activated)

JOHNSON MATTHEY & CO. LTD. *U.S. Patent 4,375,550*  
The selective hydrogenation of the nitro group in halogen-substituted aromatic nitro compound is catalysed by a platinum group metal supported on C activated with phosphoric acid. This catalyst enables halogen-substituted aromatic nitro compounds to be selectively hydrogenated without simultaneous dehalogenation.

### Catalytic Combustion

GULF RESEARCH & DEVELOPMENT CO.  
*U.S. Patent 4,378,048*

In a process for recovering energy from gas streams of low and varying heat value by catalytic combustion in substoichiometric amounts of air, two catalysts are used. The first catalyst is preferably 0.5% Pt on an  $\text{Al}_2\text{O}_3$  support, and the second 0.3% Pt and 1% Co oxide on a similar support.

### Platinum Metal Hydrogenation Catalysts

INSTITUT FRANCAIS DU PETROLE  
*French Appl. 2,505,205*

Highly dispersed Pt metal hydrogenation catalysts, especially useful for the hydrogenation of unsaturated hydrocarbons, may be obtained without haliding the catalysts, when a metal acetylacetonate is used to impregnate the support and the impregnated support is then activated by contact with  $\text{O}_2$  at 100–400°C and with  $\text{H}_2$  at 50–450°C.

### Hydrocarbon Conversion Catalysts

STE. FRANCAISE DES PRODUITS POUR CATALYSE  
*French Appl. 2,509,629*

Hydrocarbon conversion catalysts consist of a carrier such as  $\text{Al}_2\text{O}_3$  supporting 0.05–0.6% of a platinum group metal, preferably Pt or Ir, 0.05–4% In, 0.005–3% Mn or Tc and 0.1–15%  $\text{Cl}_2$ .

## HOMOGENEOUS CATALYSIS

### Olefin Hydroxylation

EXXON RESEARCH & ENGINEERING CO.  
*European Appl. 77,202*

Olefin hydroxylation to glycols using a hydroperoxide or inorganic oxidising agent in the presence of water is catalysed by  $\text{OsX}_4$ ,  $\text{Os}(\text{OH})\text{X}_3$ ,

$\text{OsOX}_4$ ,  $\text{OsONX}_4$ ,  $\text{M}_n[\text{OsX}_6]$ ,  $\text{M}[\text{Os}(\text{OH})\text{X}_3]$ ,  $\text{M}_n[\text{OsNX}_3]$  and M is a Group IA or IIA metal or a quaternary ammonium or phosphonium ion. A transition metal cocatalyst is also present.

### Combustion of Low Heating Value Gases

GULF RESEARCH & DEVELOPMENT CO.  
*U.S. Patent 4,363,361*

The substoichiometric combustion of waste gas streams is carried out in the presence of a perovskite-type catalyst in order to reduce the amount of CO in the combustion product. The catalyst used has the formula  $\text{ABO}_3$  where A is a Group IIA or lanthanide metal and B is up to 20 at.% platinum group metal and a remainder of other metals having specified atomic radii. A preferred catalyst is  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Pt}_{0.1}\text{Co}_{0.9}\text{O}_3$ .

### Platinum Metal Carborane Catalysts

UNIVERSITY OF CALIFORNIA *U.S. Patent 4,363,747*  
Catalysts having extraordinary activity for hydrogenation, hydroformylation and isomerisation reactions are Rh, Ir and Ru carborane complexes having the transition metal bonded to the pentagonal face of a dicarborane cage with two triphenylphosphine and one H ligand occupying the remaining metal ligand sites. A typical catalyst is  $[\text{closo-Bu.H}(\text{PPh}_3)_2\text{Rh}] \text{C}_2\text{B}_9\text{H}_{10}$ .

### Palladium Hydroxamate Olefin Oxidation Catalyst

INSTITUT FRANCAIS DU PETROLE  
*U.S. Patent 4,365,082*

The oxidation of olefins to unsaturated esters, such as the oxidation of ethylene to vinyl acetate, may be carried out with good selectivity and in the liquid phase in the complete absence of halide ions using a catalyst which is an organometallic Pd complex containing two identical or different hydroxamate and a carboxylate anion. A preferred catalyst is Pd phenyl benzohydroxamate.

### Hydroformylation Catalyst System

AGENCY OF INDUSTRIAL SCIENCE & TECHNOLOGY  
*U.S. Patent 4,370,258*

Highly active catalyst, which may be used to selectively obtain butyraldehyde and hexylaldehyde from hydroformylation reactions, contain Pt, a Group IVB metal halide and a bidentate ligand, such as bis(diphenylphosphino)propane, as a reaction promoter.

## FUEL CELLS

### Power Generator

TOKYO SHIBAURA DENKI K.K. *European Appl. 80,159*  
A power generator which is a stack of  $\text{H}_2$  fuel cells is designed to have an extended active life and greater physical robustness. Grooved porous C electrodes are used and the cathodes are coated with a catalytic material containing Pt.

## Fuel Cell Catalyst

UNITED TECHNOLOGIES CORP. *U.S. Patent 4,373,014*  
An improved catalyst for O<sub>2</sub> reduction at a fuel cell electrode is an alloy of Cr and Pt.

## GLASS TECHNOLOGY

### ZGS-Pd Sandwich

JOHNSON MATTHEY P.L.C. *British Appl. 2,107,378 A*  
Bushings for fibre glass manufacture and similar articles are made more cheaply for an identical mechanical strength by using composite materials. These consist of two or more layers of dissimilar noble metals bonded together. For example a layer of pure Pd may be sandwiched between layers of Pt dispersion-hardened with Pd. These composites may replace Rh-Pt alloys.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Optical Concentrator Device

U.K. SECRETARY OF STATE FOR DEFENCE  
*British Appl. 2,109,396 A*  
Dye lasers, fluorescent light activated displays and similar concentrator devices use a fluorescent dye of formula ML<sub>2</sub>Z, where M is low valency Ru, Os or Ir, L is the same or different ligand, at least one heterocyclic, and Z is an ion, such as Ru(bipy)<sub>3</sub>Cl<sub>2</sub>, Os(bipy)<sub>3</sub>I<sub>2</sub> or IrCl<sub>2</sub>(phen)<sub>2</sub>I.

### Elastically Deformable Die for Conductive Paste Printing

ROBERT BOSCH G.m.b.H. *British Appl. 2,110,162 A*  
By using an elastic deformable die it is possible to deposit patterns of electrically conducting ink on non-planar surfaces, particularly curved surfaces. The paste may contain Pt and ZrO<sub>2</sub> in a binder to produce electrochemical (Lamba probe) sensors.

### Curable Ink or Paint Containing Electrically Conductive Particles

JOHNSON MATTHEY P.L.C. *British Appl. 2,111,072 A*  
An ink which contains at least 8% of electrically conductive metal particles is based on a resin cured by free radicals. It is made u.v. curing by adding a photosensitiser and activator which is decomposed by the activated photosensitiser to give free radicals. This avoids the screening effect caused by the metallic pigment. Platinum group metal, Au and Ag particles may be present in inks and paints for electronic purposes.

### Flexible Solar Cell

KANEGAFUCHI KAGAKU KOGYO K.K.  
*European Appl. 78,541*  
A non-glass integrated solar cell capable of generating an increased open-circuit voltage consists of a metal film coated with an insulating thin film and

supporting a photovoltaic device of non-single-crystalline semiconductors. It is provided with a lower electrode which may be of Pt, Au or Ag among other materials, an upper transparent electrode of for example Sn-In oxide or Pt, on which is a comb-shaped electrode grid of, for example Pd or Ag.

### Light Duty Corrosion Resistant Contacts

JOHNSON MATTHEY P.L.C. *European Patent 82,647*  
Light duty, corrosion resistant, electrical contacts are made from an inlaid base metal or metal alloy, the inlay being made from alloys of one or more platinum group metals, Au, Ag and optional minor amounts of Cu, Ni, In and any platinum group metals not already present. A typical alloy contains 37% Au, 33% Ag and 30% Pd.

### Metal Covering of Textile Materials

A. E. BERGSTROM ET AL *European Appl. 84,300*  
Textile materials are given an ionisation treatment and then immersed in a metal sulphamate bath containing a catalyst so that metal deposits on the materials. Group VIII base metals form the coating and the catalyst is a platinum group metal, Au or Ag.

### Inks for Printed Circuit Production

AMP INC. *U.S. Patent 4,368,281*  
Ink compositions containing Pd, Pt, Ni or Cu coordination complexes are especially suitable for printing flexible polyester substrates, for example by flexographic printing. A preferred complex is Pd bisbenzo-nitrile dichloride used in a trichloroethane solvent together with TiO<sub>2</sub> and/or ferric oxide fillers.

## MEDICAL USES

### Enamel-Coated Prosthesis Materials

ERNST LEITZ WETZLAR G.m.b.H.  
*U.S. Patent 4,365,356*  
Metal implants, which may be of Pt, Au, Ag or of base metal have plasma sprayed ceramic coatings to improve adhesion to bone and also to encourage bone growth over the implant. The coatings consist of inorganic enamel matrixes carrying partially embedded particles of bio-active ceramic material.

### Platinum Complex Drugs

KUREHA KAGAKU KOGYO K.K. *U.S. Patent 4,372,890*  
Complexes LPtCl<sub>2</sub> may be used in the treatment of tumours and bacterial infections; L is ethane-1,2-diamino-1,2-dicarboxylic acid or one of its Group IA metal complexes or lower alkyl esters.

### Dental Alloys

DEGUSSA A.G. *German Offen. 3,132,143*  
Alloys compatible with ceramic materials for use in dental crowns and bridges contain 70-80% Au, 1-10% Pt, 5-15% Pd, 0.1-5% Sn, 0-5% In, 0-2% Zn and up to 10% other metals in the range 0.1-9% Ag and/or Cu, 0.05-2% Ir, Ru and/or Re, and 0.1-3% Co, Cr, Ga, Mo, Nb, Ta and/or V.