

(C<sub>6</sub>H<sub>5</sub>CN)<sub>2</sub>. In both cases, preferential formation of *trans*-pent-2-ene occurs. The reaction mechanisms involve  $\pi$ -allylic intermediates; for the Pd-catalysed reaction bis- $\pi$ -allyl complexes may also participate.

### Homogeneous Hydrogenation of Buta-1,3-diene and Ethylene Catalysed by Carbonylhydridotris(triphenylphosphine)iridium(I) and by Carbonyltrihydridobis(triphenylphosphine)iridium(III)

M. G. BURNETT, R. J. MORRISON and C. J. STRUGNELL, *J. Chem. Soc., Dalton Trans.*, 1974, (16), 1663-1671  
Spectrophotometric and kinetic studies of the individual steps in the catalytic cycle of buta-1,3-diene hydrogenated to a mixture of butenes and butane by IrH(CO)(PPh<sub>3</sub>)<sub>3</sub> and IrH<sub>3</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub> at 50°C in dimethylformamide, were quantitatively interpreted in terms of a mechanism based on the reductive elimination of butenes by Ir( $\sigma$ -C<sub>4</sub>H<sub>7</sub>)H<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>. The intermediate Ir( $\pi$ -C<sub>4</sub>H<sub>7</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> was also isolated and characterised.

### Complex Metal-Polymer Catalysts for Benzene Hydrogenation

E. N. RASADKINA, T. V. KUZNETSOVA, A. T. TELESHEV, I. D. ROZHDESTVENSKAYA and I. V. KALECHITS, *Kinet. Kataliz.*, 1974, 15, (4), 969-973  
Studies of Rh, Ir and Pd catalysts complexed with nylon showed how conditions of their preparation affect their properties in C<sub>6</sub>H<sub>6</sub> hydrogenation. Cyclohexene is formed as well as cyclohexane. The order of activity of these complexes is Ir > Pt > Rh > Pd.

## NEW PATENTS

### METALS AND ALLOYS

#### Palladium Alloy for Hydrogen Membranes

URALSKY ORDENA TRUDORAGA KRASNOGO ZNAMEI POLITEKHNICHESKY INSTITUT  
*British Patent* 1,365,271

Alloys for H diffusion contain 1-26% Ag, 1-26% Au, 0.1-0.9% Ru, 0.1-2% Al and 0.1-2.5% Pt, remainder Pd. In one example an alloy contains 75% Pd, 20% Ag, 2.5% Au, 0.5% Ru, 1% Al and 1% Pt.

### CHEMICAL COMPOUNDS

#### Synthesis of Silyl Metal Complexes

DOW CORNING CORP. *British Patent* 1,363,158  
Silyl Pt and Pd complexes are formed by reacting disilanes or hydrosilanes with Pt or Pd phosphine complexes. Thus Si<sub>2</sub>Cl<sub>6</sub> with Pd(PPh<sub>2</sub>Me)<sub>2</sub>Cl<sub>2</sub> gives Pd(PPh<sub>2</sub>Me)<sub>2</sub>(SiCl<sub>3</sub>)Cl.

## CHEMICAL TECHNOLOGY

### Morphology of Dimensionally Stable Anodes

K. J. O'LEARY and T. J. NAVIN, *Extended Abstr.*, 145th Mtg., *Electrochem. Soc.*, 1974, 74-1, (May), 603-608, abstr. 257

X-ray studies of 2:1 molar ratio solutions of Ti and Ru painted on a clean Ti substrate and fired at 100-700°C showed that below 300°C they are amorphous and above 700°C they are fully crystalline with extremely small crystals of 100-500Å. Electrical conductivity of fully crystalline solid solutions falls between the insulator TiO<sub>2</sub> and metallic conductor RuO<sub>2</sub>.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Reliability Studies of the PtSi-Ta-Au Metalisation System for Microwave Power Transistors

H. M. DAY, A. CHRISTOU, W. WEISENBERGER and J. K. HIRVONEN, *Extended Abstr.*, 145th Mtg., *Electrochem. Soc.*, 1974, 74-1, (May), 188-189, abstr. 75

X-ray and electron diffractometry studies of the Si-Ta-Pt-Au and Si-Pt layers showed formation of TaAu, Ta<sub>2</sub>Si and Ta<sub>2</sub>Pt compounds at >450°C, while PtSi formed at the Si-Pt interface at 200°C in 20 min. The ion backscattering data indicate that no further reaction takes place at the Si-Pt interface when annealed in vacuum at 700°C. Auger electron data on the Si-Ta-Pt-Au system are also obtained and discussed.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Ruthenium Dioxide Electrode Coating

ELECTRONOR CORP. *British Patent* 1,370,529  
Finely-divided RuO<sub>2</sub> having a particulate size of 0.1  $\mu$  or less dispersed in an organic polymer, resistant to degradation in an electrolytic process exhibits a low oxygen overvoltage for a surprisingly long period of time. Also a combination of finely-divided RuO<sub>2</sub> and organic polymer on an electrically-conductive substrate provides an efficient electrode for many electrochemical reactions.

## HETEROGENEOUS CATALYSIS

### Aromatic Hydrogenation

TEXACO DEVELOPMENT CORP.  
*British Patent* 1,363,179  
The hydrogenation of aromatic hydrocarbons in

the presence of S may be achieved by adding CO to the feedstock before it passes over a fluorided Pt/Al<sub>2</sub>O<sub>3</sub>.

### Deuterium from Hydrogen-containing Compounds

GULF RESEARCH & DEVELOPMENT CO.

*British Patent 1,364,714*

A vapour of a deuterium-containing hydrocarbon undergoes deuterium transfer to another hydrocarbon at high temperature in the presence of a hydrogenation-dehydrogenation catalyst, especially Pt.

### Reforming Catalyst

STE. FRANCAIS DES PRODUITS POUR CATALYSE

*British Patent 1,364,744*

Hydrocarbon reforming is catalysed by an Al<sub>2</sub>O<sub>3</sub> support carrying 0.005-1% Pt, 0.005-1% Ir and 0.05-3% Tl and/or In.

### Combination Reforming Process

ESSO RESEARCH & ENGINEERING CO.

*British Patent 1,364,875*

The naphthene content of a paraffin/naphtha feedstock is increased in contact with a Pt group metal and then the product stream is mixed with H and contacted with a support mixture of Pt with either Ir, Rh or Ru. Suitably, 0.01-2% of both metals are present on an Al<sub>2</sub>O<sub>3</sub> support.

### Trimethyl Hydroquinone Production

KURARAY CO. LTD.

*British Patent 1,365,035*

2,3,6-Trimethyl-p-benzoquinone is reduced to the corresponding hydroquinone using H in the presence of a Pd catalyst and an aliphatic ketone solvent, e.g. Pd/C plus MIBK.

### Isopropylaniline Production

ESZAKMAGYARORSZAGI VEGYIONUK

*British Patent 1,365,106*

N-Isopropylaniline is obtained when aniline and acetone are reacted in a hydrogen atmosphere at elevated temperatures and pressures using a Pt catalyst, for example, 1% Pt/Al<sub>2</sub>O<sub>3</sub>.

### Hydrocarbon Conversion Catalyst

UNIVERSAL OIL PRODUCTS CO.

*British Patent 1,366,334*

A reforming catalyst is obtained by impregnating a support (Al<sub>2</sub>O<sub>3</sub>) with a complex Sn-Pt group metal anionic species and calcining in the usual way. An acidic SnCl solution mixed with a H<sub>2</sub>PtCl<sub>6</sub> solution supplies a suitable impregnating solution.

### Saturated Hydrocarbon Isomerisation

NIPPON OIL CO. LTD.

*British Patent 1,366,784*

The isomerisation of hydrocarbons, e.g. straight chain paraffins, is catalysed by a mixture of 0.01-5% Pt or Pd and 0.01-15% halogen on a mordenite support where the halogen is intro-

duced by contact with a fluorohalohydrocarbon, e.g. CHCl<sub>2</sub>F.

### Epoxy Spirolactones

S. D. SEARLE & CO.

*British Patent 1,368,731*

Spirolactones are produced in a process where an epoxy androstene furandione is hydrogenated over Pd/C to give the corresponding androstane derivative.

### Platinum-Cobalt Catalyst Bed for Flameless Catalytic Heater

BRUEST INDUSTRIES INC. *U.S. Patent 3,802,856*

A catalyst bed unit employing a measured amount of cobalt in conjunction with Pt forms the fuel-reactive catalyst of the unit to render the heater capable of operation at low CO emission levels. The catalyst is applied to its support by dissolving chloroplatinic acid and cobalt nitrate in a solution of methanol and water, spraying the mixture on to the support and heating the unit to reduce the H<sub>2</sub>PtCl<sub>6</sub> and Co nitrate to Pt and Co metals.

### Catalyst of Zinc Lanthanide Exchanged Zeolite

MOBIL OIL CORP.

*U.S. Patent 3,804,780*

Pt and Pd catalysts may be supported on a crystalline zeolite having 6-13% lanthanide cations and less than 2.5% Zn cations.

### NO<sub>x</sub> Abatement

JOHNSON MATTHEY & CO. LTD.

*U.S. Patent 3,806,582*

A process is described for the purification of gases containing NO<sub>x</sub> formed in the manufacture of HNO<sub>3</sub>. A gas containing the oxides and including O and a gaseous reducing fuel, is passed at a temperature above the ignition temperature of the gas and the fuel through a catalyst comprising an inert ceramic material impregnated or coated with a mixture or alloy of Pt and Rh metals in which Rh ranges from 20-50% by weight but is preferably present to the extent of 35% by weight of the catalytic metal content of the catalyst.

### Preparing Amino-substituted Phosphonates

THE GATES RUBBER CO.

*U.S. Patent 3,813,456*

The preparation of amino-substituted phosphonates from their corresponding cyano-substituted phosphonate precursors, consists of hydrogenating the cyano-substituted phosphonates in the presence of NH<sub>3</sub> and Rh catalyst.

### Ruthenium NO<sub>x</sub> Removal Catalyst

FORD MOTOR CO.

*U.S. Patent 3,819,536*

A fixing compound, selected from an alkaline earth material or a rare earth material which decomposes to an oxide of the material, is deposited on a catalytic support. A hydrated, halogenated Ru compound which reduces to Ru is also deposited on the catalytic support. The materials on the support are heated in a reducing

atmosphere to form the Ru metal. After the reducing step the materials are fixed by heating them to a ruthenate-forming temperature.

### Platinum Reforming Catalyst

STE. FRANCAIS DE PRODUITS POUR CATALYSE  
*French Appl.* 2,196,192

The catalyst, for use in hydrocarbon reforming, has an  $\text{Al}_2\text{O}_3$  support, 0.005–1.0% Pt, 0.005–1.0% Ir and 0.005–5.0% Nb.

### Acetic Acid Production

BASF A.G. *German Offen.* 2,303,271

Acetic acid, optionally with methyl acetate, is obtained by the reaction of methanol with CO in the presence of Co catalysts promoted with Br and/or I and Pd, Pt, Ru, Ir or Cu.

## HOMOGENEOUS CATALYSIS

### Carbon Monoxide Copolymerisation Catalyst

SHELL INTERNATIONALE RESEARCH MIJ. B.V.  
*British Patent* 1,362,908

High molecular weight polymers are produced from CO and other monomers, e.g.  $\text{C}_2\text{H}_2$ , in the presence of an aryl phosphine-palladium halide complex, e.g.  $(\text{PPh}_3)_2\text{PdCl}_2$  or  $\text{Pd}(\text{PR}_3)_4$ .

### Cationic Platinum Catalysts

BP CHEMICALS INTERNATIONAL LTD.  
*British Patent* 1,362,997

New catalysts for alcohol carbonylation and other reactions are complexes of univalent or trivalent Rh or Ir with acetonitrile, benzonitrile, butyl isocyanate, benzene, toluene, phosphite or phosphine; the anion must be a phosphate, sulphate, perchlorate, borate, iodate or bromate. A typical catalyst is  $\text{Rh}(\text{P}(\text{O}Ph)_3)_4\text{BPh}_4$ .

### Silane Production

DOW CORNING CORP. *British Patent* 1,363,157

Pt, Pd and Ni phosphine complexes are used to catalyse the reaction of a  $\text{Si}_2\text{Cl}_2$  and a halide to form mixed substituted silanes. For example,  $\text{PhSiCl}_3$  is prepared by the reaction of  $\text{Si}_2\text{Cl}_2$  and  $\text{PhCl}$  in the presence of  $\text{Pd}(\text{PPhMe}_2)_2\text{Cl}_2$ .

### Unsaturated Organosilicon Compounds

ČESKOSLOVENSKA AKADEMIE VED  
*British Patent* 1,363,317

Silane addition to a diene is catalysed by an inorganic Pd compound or organic complex. For example, the addition of triethoxysilane to butadiene is catalysed by bis(allyl)Pd chloride.

### Cyanobenzoic Acid Hydrogenation

ASAHI KASEI K.K.K. *British Patent* 1,368,415

p-Aminomethyl benzoic acid is produced in one step by the reaction of an alkyl ester of p-cyanobenzoic acid in aqueous alkaline medium containing a catalyst, e.g. Rh, Ru,  $\text{RuO}_2$ ,  $\text{RhO}_2$ , etc.

### New Rhodium Complex

JOHNSON MATTHEY & CO. LTD.  
*British Patent* 1,368,431

New complexes of Rh(I) for use in catalysing hydrogenation, oxidation, decarbonylation, isomerisation, hydroformylation and other reactions are obtained by adding excess of an arsine, phosphine, stibine, sulphide or amine stabilising ligand (susceptible to oxidation) to a Rh(II) carboxylate solution protonated by an acid. The complexes are of the type  $\text{Rh}(\text{CO})(\text{PPh}_3)_3\text{BF}_4$ , e.g. prepared from a rhodium acetate ( $\text{HBF}_4$ ) phosphine solution by bubbling through carbon monoxide.

### Palladium Complex in Oligomer Production

MITSUBISHI CHEMICAL INDUSTRIES LTD.  
*British Patent* 1,369,128

A chain oligomer is produced from a vinyl or vinylidene aromatic compound in the presence of a Pd compound, a compound containing a fluoro complex or perchlorate anion and a trivalent organic P compound, e.g. methallyl Pd chloride, tributyl phosphine and Ag chlorate or borofluoride.

### Producing Oligomers of Unsaturated Compounds

MITSUBISHI CHEMICAL INDUSTRIES LTD.  
*U.S. Patent* 3,803,254

Pd phosphine, arsine and stibine complexes, e.g.  $[\text{PdL}_2(\text{PPh}_3)][\text{BF}_4]_2$ , where L is benzonitrile, are used to oligomerise styrene and other unsaturated compounds.

### Ruthenium Complexes

RHONE-POULENC S.A.  
*U.S. Patents* 3,804,868 & 3,804,869

New Ru complexes of the formula  $\text{Ru}(\text{diket})_2\text{L}_n$  in which (diket) represents a bidentate ligand derived from a  $\beta$ -diketone and L is a tertiary phosphine ligand, are useful as catalysts in, for example, isomerisations (such as the REPPE synthesis), hydrogenations and dimerisations (such as the hydrodimerisation of acrylonitrile to adiponitrile).

### Ruthenium(II) Complexes as Selective Hydrogenation Catalysts

PHILLIPS PETROLEUM CO. *U.S. Patent* 3,804,914

Cyclic polyenes are selectively hydrogenated to cyclic monoenes in the presence of a Ru(II) catalyst complex having the general formula  $\text{L}_n\text{RuX}_m$  where L is a ligand, X is a halogen or hydrogen, n is 2, 3 or 4, m is 2 or 3 and the sum of  $n+m$  is 4, 5 or 6, e.g.  $(\text{Ph}_3)_2(\text{CO})_2\text{RuCl}_2$ .

### Platinum Catalyst for Siloxane Curing

WACKER-CHEMIE A.G. *U.S. Patent* 3,814,731  
Polyorganosiloxanes in non-stick coatings are cured with a reaction product of  $\text{H}_2\text{PtCl}_6$  and a ketone.

## Production of Carboxylic Acids

MONSANTO CO.

*U.S. Patents* 3,816,488 & 3,816,489

An improved process for the production of carboxylic acids by the reaction of ethylenically unsaturated compounds with CO and water uses catalyst compositions consisting of Rh compounds and complexes together with an iodide promoter in critical proportions, e.g. RhCl<sub>3</sub> promoted with HI, and Ir compounds and complexes together with an iodide promoter in critical proportions, e.g. IrCl<sub>3</sub> and HI.

## Preparing Linear Fatty Acids

TEXACO INC.

*U.S. Patent* 3,819,669

A process for preparing linear fatty acids and esters from alpha olefins and CO uses homogeneous Pt complexes, e.g. a Pt(AsPh<sub>3</sub>)<sub>2</sub>-SnCl<sub>2</sub> system.

## CHEMICAL TECHNOLOGY

### Electrolysis Electrodes

HOOKEER CHEMICAL CORP. *British Patent* 1,366,429

A new design of electrode has a sandwich structure in which the outer layers consist of slotted plates of a valve metal, e.g. Ti, coated with a Pt group metal or metal oxide (except Os).

## GLASS TECHNOLOGY

### Ceramic Inductor

W. L. MUCKELROY

*U.S. Patent* 3,812,442

An inductor consists of a tape of ceramic material carrying a helical path of metal film, e.g. a Pt-Au-glass paste film.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Electrodes for Acid Electrolytes

BADISCHE ANILIN- & SODA-FABRIK A.G.

*British Patent* 1,360,255

Two electrically conducting bodies, e.g. Pt foil and a metal electrode base, are cemented together by an ethylene-unsaturated acid copolymer filled with an electrically conducting medium, e.g. Au, Pt, silvered Ti, gilded Ti, platinised Ti, etc.

### Electron Discharge Heater

G.T.E. SYLVANIA INC. *British Patent* 1,366,007

A dark heater coating consists of Al, Zr or Be oxide coated with 2-2.5% W which is protected from oxidation by Pt or Ir.

### Lead-based Alloys for Electrode

BADISCHE ANILIN- & SODA-FABRIK A.G.

*British Patent* 1,369,707

Pb-based alloys used for solid or grid electrodes are further improved in their efficiency and life

when they contain Pd as a component. A preferred Pb alloy contains 0.05 to 0.15% of Cu, 0.05 to 0.15% of Sn and 0.05 to 0.2% of Pd. In one example 0.1% of each of these was used.

## Bilevel Thin Film Integrated Circuit

BELL TELEPHONE LABORATORIES INC.

*U.S. Patent* 3,811,973

Bilevel thin film circuits having Au metallised through holes require protection from attack by Au conductor etchants. A new procedure for this involves plating an etch stop such as Rh or Pt on the walls of the through holes and around the entrance and exit ports. Since Rh plating is normally required in the fabrication of such circuits for solderable components, the through hole protection and Rh plating may be performed simultaneously.

## Gold Alloy Metallisation for Capacitor Electrodes

E. I. DU PONT DE NEMOURS & CO.

*U.S. Patent* 3,817,758

Powder compositions useful in making ceramic capacitors electrodes and capacitors contain specific alloys of 5-15% Pt, 15-30% Pd and 60-80% Au.

## TEMPERATURE MEASUREMENT

### Implantable Thermopiles

NUCLEAR BATTERY CORP.

*British Patents* 1,370,382-1,370,386

Thermopiles for use in human bodies contain a semiconductor thermoelectric wired up using a wire made of Au, Ag, Pt or their alloys.

### Temperature Measurement

BRITISH IRON & STEEL RESEARCH ASSOCIATION

*British Patent* 1,370,465

Temperatures in steelmaking furnaces, for example, are measured by a couple formed by dissimilar metal conductors placed side-by-side in a refractory insulating matrix with a conducting path between their ends in the furnace. In one example, Pt and Pt-Rh conductors are embedded in magnesia.

### High Temperature Thermocouple Alloy Systems

U.S. ATOMIC ENERGY COMMISSION

*U.S. Patent* 3,817,793

A thermocouple system capable of delivering a substantially linear EMF response as a function of temperature up to 1800°C in a thermal neutron environment has a positive leg and a negative leg consisting of a Cr-base binary alloy having sufficient ductility to be drawn into wire form; the alloy contains 15-25 at.% Ru, 15-20 at.% Os and the balance Cr.