

### Reactive Transition Metal Dinitrosyl Complexes. Synthetic Uses and Catalytic Properties

B. L. HAYMORE and J. A. IBERS, *J. Am. Chem. Soc.*, 1974, **96**, (10), 3325-3327

Series of reactions and experiments of Rh, Ir dinitrosyl complexes showed that they are very reactive and that the conversion of NO and CO into NO<sub>2</sub> and CO<sub>2</sub> is catalytic and general in scope. The reactions implicate transition metal dinitrosyls as the important species in the reduction of NO by CO.

### Photochemical Activation of IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub> Hydrogenation Catalysts

W. STROHMEIER and G. CSONTOS, *J. Organometal. Chem.*, 1974, **72**, (2), 277-282

Under weak U.V. radiation the activity of IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub> as a hydrogenation catalyst is increased approximately fortyfold. Reactive intermediates are formed in both reversible and irreversible steps. Once the active intermediate compound has been produced in the irreversible step, rapid hydrogenation proceeds even in the absence of radiation.

### Catalytic Action of Ruthenium Compounds in the Process of Styrene Oxidation

M. E. PUDEL' and Z. K. MAIZUS, *Neftekhimiya*, 1974, **14**, (3), 412-416

RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> additions catalyse the oxidation of styrene and increase the yield of styrene oxide. The styrene oxide:benzaldehyde concentration ratio rises with increased temperature and decreased O<sub>2</sub> concentration in the oxidising gas.

### On the Catalytic Properties of Blue Complexes of Ruthenium

L. KH. FREIDLIN, E. F. LITVIN and K. G. KARIMOV, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1974, (4), 821-824

Blue Ru chloride complexes were produced by reducing Ru(IV) compounds with H<sub>2</sub> in the presence of Ru black. Ru chloride complexes promote C=C bond migration and *cis-trans*

isomerisation of olefins not catalysed in hydrogenation. These complexes catalyse selective hydrogenation and isomerisation of dienes.

### Stoichiometric Hydrogenation of Olefins Using HRuCl(PPh<sub>3</sub>)<sub>3</sub> and Formation of an *ortho*-Metallated Ruthenium(II) Complex

B. R. JAMES, L. D. MARKHAM and D. K. W. WANG, *J. Chem. Soc., Chem. Commun.*, 1974, (11), 439-440

Studies of stoichiometric hydrogenation of olefins using HRuCl(PPh<sub>3</sub>)<sub>3</sub> in the absence of H<sub>2</sub> showed formation of the dimer [(Ph<sub>3</sub>P)ClRu(*o*-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)]<sub>2</sub> which reacted with H<sub>2</sub> and HCl, to yield catalytically important bisphosphine complexes RuXCl(PPh<sub>3</sub>)<sub>2</sub> (X=H, Cl).

## GLASS TECHNOLOGY

### A New Design of Nozzle for Bubbling Glass

T. M. GALIEVA and S. I. MATYUSHA, *StekloKeram.*, 1974, (5), 16-17

The nozzle of the glass bubbling tube is covered with Pt, both in the old design and in the new design, which has wider bores in the corundum twin-channel tubing.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Reaction Rates for Pt on GaAs

D. J. COLEMAN, W. R. WISSEMAN and D. W. SHAW, *Appl. Phys. Lett.*, 1974, **24**, (8), 355-357

The rate at which GaAs reacts with Pt was determined at 300-400°C. The amount of GaAs reacted was determined by measurement of the movement of the original Pt Schottky-barrier contact into the GaAs. The amount of GaAs reacted is a function of annealing time at several different temperatures. The reaction follows a parabolic rate law with activation energy of 1.6eV. Some changes in the electrical characteristics of the Schottky barrier are observed.

## NEW PATENTS

### CHEMICAL COMPOUNDS

#### Palladium Acetylacetonate of Low Chlorine Content

BAYER A. G. *U.S. Patent* 3,787,462

A high purity Pd acetylacetonate is obtained by precipitating a Pd compound from an aqueous alkali PdCl<sub>2</sub> solution with an alkali metal hydroxide, converting the precipitate to the Pd acetylacetonate with acetylacetone and washing and drying the acetonate.

#### Compounds of Ruthenium

JOHNSON MATTHEY & CO. LTD.

*U.S. Patent* 3,793,355

A composition of matter has the general formula MM'M"XA<sub>6</sub>LL'L" where M, M' and M" are the same or different transition metals selected from the second or third series of the periodic table; X is O, S, N, P or B; A is an anionic element or group and L, L' or L" are neutral or anionic ligands. A preferred compound is Ru<sub>3</sub>O(OCOMe)<sub>6</sub>(PPh<sub>3</sub>)<sub>3</sub> and generally the Ru carboxylates are used as homogeneous catalysts.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Electrodeposition of Ruthenium

INTERNATIONAL NICKEL CO. INC.

*U.S. Patent 3,793,162*

An electroplating bath and process for electroplating Ru is prepared by dissolving  $\text{Ru}_2\text{N}(\text{OH})_6 \cdot n\text{H}_2\text{O}$  in  $\text{H}_2\text{SO}_4$  or  $\text{H}_2\text{NSO}_3\text{H}$  and adjusting the pH to 4 or less.

### Electroless Plating

TORAY INDUSTRIES INC. *U.S. Patent 3,801,368*

In an electroless plating method Pd or Au is deposited on a substrate in vacuum and then the substrate is electrolessly plated using the previously deposited Pd or Au as the catalyst.

## LABORATORY APPARATUS AND TECHNIQUE

### pH Meter Electrodes

GENERAL ELECTRIC CO.

*British Patents 1,353,209, 1,353,210*

A reference electrode, including a Ag wire coated with AgCl is positioned within an insulating tube the opposite end of which is surrounded with Pd coated with Pd oxide.

## HETEROGENEOUS CATALYSIS

### Dehydrogenation Catalyst

UNIVERSAL OIL PRODUCTS CO.

*British Patent 1,351,393*

A dehydrogenation catalyst is produced by impregnating  $\text{Al}_2\text{O}_3$  with a solution containing a Ge compound, a Pt group metal compound, a halide and an alkali metal compound. The product is steamed to reduce the halogen content to less than 0.1%. The impregnated and steamed support is dry heated at 204–649°C, reduced and sulphided. Pt and Pd are preferred.

### Aminocyclohexyl Compound Production

BADISCHE ANILIN- & SODA-FABRIK A. G.

*British Patent 1,351,487*

Bis(aminocyclohexyl)alkanes or ethers are produced by hydrogenation or the corresponding aminophenyl compounds over a suspended catalyst which may be Ru.

### Hydroreforming Catalysts

CIE, FRANCAISE DE RAFFINAGE

*British Patent 1,351,562*

A new hydroreforming catalyst consists of a refractory inorganic oxide support, e.g.  $\text{Al}_2\text{O}_3$ , having a surface area of more than 15 m<sup>2</sup>/g and

a pore volume of more than 0.1 cm<sup>3</sup>/g carrying 0.02–2% Pt (preferably 0.1–0.7%), 0.02–2% Ir (preferably 0.1–0.7%) and 0.02–2% Sn.

### Hydrogenation Catalysts

DU PONT OF CANADA LTD. *British Patent 1,352,737*

Butyrolactam and valerolactam respectively are obtained by hydrogenation of succinimide and glutarimide in the presence of a catalyst, e.g. Pt, Pd or Re, optionally supported.

### Preparation of Rhodium-containing Catalyst

SHELL INTERNATIONALE RESEARCH MIJ. N.V.

*British Patent 1,354,778*

Rh containing catalyst, suitable for the ring-opening and saturation of cyclic hydrocarbons, is produced by mixing  $\text{SiO}_2$  and a Rh-cation-containing solution so that ion-exchange takes place, removing the liquid and drying the ion-exchanged  $\text{SiO}_2$ .

### Platinum-Lead Catalysts

ASAHI KASEI K.K.K.

*British Patent 1,356,464*

Pt-Pb catalysts supported on a carrier such as  $\text{Al}_2\text{O}_3$  are regenerated by applying HCl and/or  $\text{HNO}_3$  solutions and calcining the catalysts. The catalysts may contain further metals, among them Ag, Au and Pt group metals.

### Catalytic Reforming

BRITISH PETROLEUM CO. LTD.

*British Patent 1,356,634*

Hydrocarbon reforming is catalysed by a supported mixture of a Pt group metal and As. The support, such as  $\text{Al}_2\text{O}_3$ , must be free from alkali and alkaline earth metals. The Pt (or other Pt-group metal) content is 0.01–5% and the As content is 5–35 at.% of the Pt+As content.

### Catalytic Reforming

UNIVERSAL OIL PRODUCTS CO.

*British Patent 1,359,728*

A relatively lean octane hydrocarbon fraction is reformed using a supported Pt-Re catalyst in two stages with water excluded in the first, but not the second stage.

### Methanation of Carbon Monoxide and Carbon Dioxide

INSTITUTE OF GAS TECHNOLOGY

*U.S. Patent 3,787,468*

The preferential, selective and sequential methanation for reaction of gases containing CO or  $\text{CO}_2$  in the presence of  $\text{H}_2$ , using catalysts of Rh and Ru metals or alloys with Pt is improved with W oxide. Typically Ru and  $\text{WO}_x$  in a 85:15 ratio or Pt, Rh and  $\text{WO}_x$  in a 42.5:42.5:15 ratio are used. x is unknown.

### Selective Hydrogenation of Hydrocarbons

P. BERNUSSET

*U.S. Patent 3,787,515*

Unsaturated impurities in the purification of

ethylenic gases are removed by selective hydrogenation with a Pd catalyst having an addition of V as a promoter.

#### Preparation of Catalysts

ESSO RESEARCH & ENGINEERING CO.  
*U.S. Patent 3,789,020*

A catalyst is formed from a mixture of one or more Group VIII metals with an optional Group IB metal, e.g. Pt and Cu, deposited on particles of a support such as  $Al_2O_3$ , mixed with further uncoated particles of support.

#### Reforming Catalyst

PHILLIPS PETROLEUM CO. *U.S. Patent 3,789,024*

An improved catalyst has refractory-supported Pt promoted with both Ir and Ga and exhibits increased activity and selectivity characteristics for the dehydrocyclisation and reforming of hydrocarbons. In one example,  $Al_2O_3$  promoted with Pt, Ir and Ga is used in the conversion of *n*-heptane to benzene and toluene with substantial conversion at high selectivity.

#### Tetrametallic Hydrocarbon Conversion Catalyst

UNIVERSAL OIL PRODUCTS CO.  
*U.S. Patent 3,790,473*

A catalytic composite contains Pt or Pd, Ir, Re and Sn on a porous carrier material. It is used mainly in the conversion of hydrocarbons, particularly in the reforming of a gasoline fraction. A specific example of this catalytic composite is a combination of Pt, Ir, Re, Sn and a halogen with  $Al_2O_3$  carrier material in amounts to supply approximately 0.01–2% Pt, 0.01–2% Ir, 0.01–2% Re, 0.01–5% Sn and 0.1–3.5% halogen.

#### Preparation of Organic Dinitriles

KURASHIKI RAYON CO. LTD. *U.S. Patent 3,790,617*

A process for preparing organic dinitriles by the dimerisation of acrylonitrile consists of reacting acrylonitrile with  $H_2$  in a gaseous phase at 100–450°C under a total pressure of 1–20 atm by using as catalyst Ru metal or a Ru compound reducible to Ru metal under reaction conditions. The catalytic activity of the catalyst can be increased by addition of an alkali metal hydroxide or a mixture of a halide of Ni, Cr, Mo or W with an organic P compound.

#### Combination Reforming Process

ESSO RESEARCH & ENGINEERING CO.  
*U.S. Patent 3,791,961*

A conventional naphthene dehydrogenation catalyst, such as a Pt-halogen/ $Al_2O_3$  catalyst, is used in the initial zone or reactor in a catalytic reforming process; the tail zone or reactor contains a supported Group VIII polymetallic catalyst with platinum as one of the metallic components. In a preferred embodiment, the tail zone contains a Pt-Ir catalyst on a porous support such as  $Al_2O_3$ .

#### Preparation of Acrylic and Methacrylic Acids

NATIONAL DISTILLERS & CHEMICALS CORP.  
*U.S. Patent 3,792,086*

Acrylic or methacrylic acids are selectively produced in a single step process involving the vapour phase oxidation of propylene or isobutylene, respectively, at temperatures of up to 300°C and in the presence of a catalyst composition containing  $H_3PO_4$  and Pd metal.

#### Reforming Catalyst

STE. FRANCAISE DES PRODUITS POUR CATALYSE  
*U.S. Patent 3,793,232*

A catalyst for the conversion of hydrocarbons, particularly for reforming reactions, has  $Al_2O_3$  base supporting on the following metals: 0.005–1% Pt, 0.005–1% Ir and 0.05–3% Tl or In. Optionally the catalyst may further contain from 0.1–10% of a halogen and up to 10% of Zn.

#### Olefin Hydroisomerisation Process

UNIVERSAL OIL PRODUCTS CO.  
*U.S. Patent 3,796,766*

Olefins are hydroisomerised utilising a catalytic composite containing a Pt group component and a Group IVA metallic component combined with a carrier material of  $Al_2O_3$  and a finely divided crystalline aluminosilicate such as mordenite. The active metals may be Pt and Ge.

#### Reforming with Platinum and Tantalum or Niobium Catalyst

BRITISH PETROLEUM CO. LTD.  
*U.S. Patent 3,799,867*

A catalyst of 0.01–5% Pt on a refractory support also contains 0.01–5% of Ta or Nb. The support is preferably  $Al_2O_3$  which may contain halogen. The Ta or Nb may be added at any convenient stage in the catalyst preparation, including adding it as a chloride or fluoride during the preparation of the support.

#### Multimetal Powder Alloy Catalyst

STAMICARBON N.V. *Dutch Appl. 73.16236*

An alloy is formed from a complex of two metals or their compounds by reduction in situ of particles on a support. Thus Ge and Pd salts can be deposited on  $Al_2O_3$  and reduced to form a Ge-Pd alloy.

## HOMOGENEOUS CATALYSIS

#### Hydroformylation and Hydrogenation Catalysts

JOHNSON MATTHEY & CO. LTD.  
*British Patent 1,357,735*

Gaseous olefins are reacted with  $H_2$  and CO (or  $H_2$  alone) in the absence of solvent but in the presence of a liquid As or Sb-containing stabilising donor ligand using as catalyst a hydrido

carbonyl complex of Rh including an As- or Sb-containing ligand. An example of the catalyst is  $\text{RhH}(\text{CO})_2[\text{AsPh}_3]$ .

### Formylindane Production

BADISCHE ANILIN- & SODA-FABRIK A.G.

*British Patent 1,358,081*

1- and 2-formylindanes are produced by the hydroformylation of indene in the presence of a Rh carbonyl complex such as  $\text{Rh}(\text{CO})(\text{PPh}_3)_2\text{Cl}$ .

### Process for Producing Acyloxydodecatrienes

MITSUBISHI CHEMICAL INDUSTRIES LTD.

*U.S. Patent 3,789,066*

Acyloxydodecatrienes are produced by reacting an octatriene, a butadiene and a carboxylic acid in the presence of a catalytic amount of a divalent Pd compound selected from organic acid salts of Pd (II), chelate complexes of Pd (II) and Pd nitrate.

### Olefin Isomerisation and/or Hydrogenation

PHILLIPS PETROLEUM CO. *U.S. Patent 3,793,257*

Ru hydride complexes containing tertiary phosphine, arsine, or stibine ligands are employed as catalysts for isomerisation and/or hydrogenation of olefins. Terminally unsaturated olefins are selectively isomerised to internally unsaturated olefins by complexes that contain N or  $\text{NH}_3$ , e.g.  $(\text{tribenzyl arsine})_3\text{RuH}_2(\text{NH}_3)$ .

### Rhodium Catalysts

JOHNSON MATTHEY & CO. LTD.

*U.S. Patent 3,794,671*

Nonhalogen or pseudo-halogen coordination complexes of Rh(I) containing a stabilising donor ligand are made by adding a compound which acts as a stabilising donor ligand to a solution of Rh (II) carboxylate protonated by an acid. The complexes with arsines, phosphines, etc. are useful catalysts. One example is  $\text{Rh}(\text{OCOMe})(\text{PPh}_3)_3$ .

### Bidentate Rhodium Coordinators

INSTITUT FRANCAIS DU PETROLE

*U.S. Patent 3,798,241*

Bidentate coordinators of the formula  $\text{R}_2\text{X}-\text{R}'-\text{YR}_2$ , in which X and Y are P, As, Sb or N, R is a hydrocarbon group containing an asymmetric C atom and the R groups are hydrocarbon radicals, may be associated with Rh complexes to yield hydrogenation catalysts useful in asymmetric synthesis, e.g. in the synthesis of optically active aminoacids or amines. For example  $\text{Rh}_2\text{Cl}_2(\text{cyclooctene})_4$  may be used with a diphosphinotartrate  $\text{Ph}_2\text{PCH}_2-\text{CH}(\text{OMe})-\text{CR}_2\text{PPh}_2$ .

### Producing Acyloxydodecatrienes

MITSUBISHI CHEMICALS INDUSTRIES LTD.

*U.S. Patent 3,798,260*

Acyloxydodecatriene is produced by reacting an octatriene, butadiene and a carboxylic acid in the

presence of a catalytic amount of Pd or Pd compound and an amine.

## CHEMICAL TECHNOLOGY

### Layered Electrode

METALLGESELLSCHAFT A.G. *U.S. Patent 3,788,968*

An electrode, especially useful as an anode in the electrolysis of alkali metal chlorides, includes a graphite body, a first surface covering of a hard ceramic such as Ti carbide or Ti nitride and at least one metal and/or metal oxide of the Pt-group and a second oxide coating which is electrically porous and resistant to the electrolysis conditions. Ru/Ru oxide are used in one example.

### Matrix Electrode

DIAMOND SHAMROCK CORP. *U.S. Patent 3,798,063*

Finely divided  $\text{RuO}_2$  serves as an efficient and long-lived electrocatalyst when dispersed in a polymer matrix chemically and mechanically inert to an electrolyte. When applied to a substrate, generally an electrically conductive substrate, an electrode, particularly suited for use as an anode at which  $\text{O}_2$  is evolved, is obtained. A coating of polyvinylidene fluoride containing  $\text{RuO}_2$  having a particle size of less than 0.1 micron on a Ti substrate is one example.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Semiconductor Contacts

R.C.A. CORP.

*British Patent 1,353,975*

A semiconductor surface is sputter etched in the presence of a backing plate so that the two surfaces provide the components of an alloy layer. For example a silicon semiconductor and a Pt backing plate become coated with Pt silicide.

### Ceramic Capacitors Metallisation

E.I. DU PONT DE NEMOURS & CO.

*U.S. Patent 3,798,516*

Metallising compositions with alloys of three or more metals are used in making ceramic capacitor electrodes. The alloys have a critical surface area. The metals of the alloy are Pd, Pt and Au. The metallising compositions are especially suitable for producing capacitors on ceramic dielectric substrates which contain  $\text{Bi}_2(\text{SnO}_3)_3$ .

## TEMPERATURE MEASUREMENT

### Thermocouple

UNITED STATES STEEL CORP.

*British Patent 1,352,743*

A conventional Pt thermocouple forms part of an electrolytic apparatus for the determination of oxygen in e.g. molten steel.