ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Effect of Helium, Iron, and Platinum Implantation on the Absorption of Hydrogen by Iron

Ion beam implantation can reduce H₂ entry into Fe, and thus preserve the mechanical properties. Pt greatly reduces H₂ entry via a catalytic effect of the H₂ evolution reaction when Pt is on the surface. The effectiveness of implanted Pt is increased by controlled selective dissolution of Fe which increased surface concentration of Pt. Selective dissolution of Fe from Pt-implanted Fe surface layer may involve some Pt and Fe interdiffusion.

A Re-examination of the Structure and Properties of Pt-SiO₂ Cermet Films

The conventional model of a cermet in the dielectric regime, metallic islands in a dielectric matrix, was shown to be unsuitable for cermets made by sputtering Pt-SiO₂ composites in an Ar-O₂ plasma. A significant proportion of the metal is incorporated into the dielectric matrix, and the compositional fluctuations appear to be more gradual than is consistent with the conventional metal island model. This interpretation is further supported by the a.c. properties of the Pt-SiO₂ cermet films.

Adsorption, Electrochemical and Electrocatalytic Properties of Metallurgical Alloys Platinum-Tin

Adsorption properties of Pt-Sn alloys for H₂ and O₂ and organic substances, and electrocatalytic properties during the oxidation of methanol and formic acid were studied in H₂SO₄ by a potentiodynamic impulse method. The addition of Sn to Pt-Sn alloy showed no noticeable promoting effect during electro-oxidation.

Diffusivity of Hydrogen in Dilute Alloys of Copper and Niobium in Palladium

The diffusion coefficients for H₂ into Pd-Cu and Pd-Nb alloys containing 0-10at.% Cu and Nb were measured between 0 and 50°C by an electrochemical technique. The H₂ content was <1at.% and the diffusivity of H₂ was decreased remarkably by adding Nb. Cu also decreased the H₂ diffusivity but less than Nb. For Pd-6.5at.%Nb a measurable change in activation energy of diffusion was observed.

Hydrogen Permeability of Modified Membranes from Pd-Ag and Pd-Ni Alloys


Studies were made of H₂ permeability of 20wt.%Ag-Pd and 6wt.%Ni-Pd membranes with surfaces modified by the deposition of a thin layer of catalytic components of Pd, Pb or Ru. Surface processes limit the H₂ transfer in Ag-Pd membranes 50-100 μm thick; in Ag-Pd membranes 254 μm thick, and in Ni-Pd membranes 100 μm thick; the limiting process is H₂ transfer through the bulk of the alloy.

Free Energy of Formation of PdO by Impedance Dispersion Analysis


The sharp increase in low frequency impedance at a Pd/solid electrolyte interface below the thermodynamic transition temperature has been used to determine the free energy of formation for PdO. This is utilised in developing a new generation of absolute oxygen monitors.

Photoelectrochemical and Solid-State Properties of LuRhO₃


Rare-earth rhodates of the distorted perovskite structure are semiconductors with a band gap of 2.2 eV. They may be doped either n or p type. With ceramic p-type LuRhO₃ as the cathode and n-type TiO₂ as the anode of an electrolytic cell sufficient photopotential is developed both to photoelectrolyse H₂O in sunlight with no externally applied potential and to generate power simultaneously.

Ruthenium and Iridium Oxidation in Air


Oxidation of Ru and Ir was studied in air at temperatures of up to 1000°C on metal powder samples 0.05-0.075 mm in diameter, prepared by calcination of [NH₄]₂RuCl₄ and [NH₄]₂IrCl₄ in H₂ at 500°C followed by cooling in Ar to room temperature. The finely dispersed Ru and Ir metals were extremely active during the oxidation, yielding corresponding dioxides.


42
CHEMICAL COMPOUNDS

Nickel, Palladium and Platinum; Annual Survey Covering the Year 1978
This extensive survey covers preparation, structure, some reactions and novel features of organic complexes of Pt, Pd and Ni. (439 Refs.)

Organometallic Intermolecular—Coordination Compounds Containing a Phosphorus Donor Ligand
A review is given of organometallic intermolecular co-ordination compounds, including platinum group metals, containing a P donor ligand. It is shown that these compounds are also able to form a five-membered ring structure. The literature is covered to July 1979. (168 Refs.)

PdB2O4, the First Palladium Borate
W. DEPAERIE, H. SCHMID and F. HAINSSLER, Naturwissenschaften, 1980, 67, (9), 456
PdB2O4 was prepared at 40kbar pressure and 800°C from a 1:1 mixture of Pb(NO3)2H2O and B2O3. The PdB2O4 crystals were dark brown to black, idiomorphic and isotypic with CuB2O4. Until now PdB2O4 has been unknown.

ELECTROCHEMISTRY

Catalytic Decomposition of Hydrogen Peroxide on Oxidised Platinum in Sulphuric Acid
Studies of the effect of pH values on the rate of catalytic decomposition of an acidic solution of H2O2 on oxidised Pt were performed in 96–98% H2SO4 at 20–23°C. It is shown that oxidising of Pt speeds up the decomposition of the solution in the pH region corresponding to the potential of the zero order of the catalytic surface.

O2 Electrocataysis on Thin Film Metallic Oxide Electrodes with the Delafossite Structure
Thin film electrodes of PrCoO2, PdCoO2, PdRhO2, and PdCrO2, delafossite-type oxide are good electrocatalysts for O2 reduction and O2 evolution in NaOH. O2 reduction activity correlates with the noble metal ratio (Pt >> Pd, Rh >> Cr). The amorphous film electrodes were prepared by r.f. sputtering from metal alloy targets. The delafossite phase forms on annealing in air or O2 at 700–850°C. The thin films are metallic with p ~ 10–14Ω cm.

Effect of Heat Treatment of Ti Substrate on Service Life of Ti-Supported IrO2 Electrode in Mixed Aqueous Solutions of H2SO4, (NH4)2SO4 and NH4F
The effect of heat treatment of the Ti substrate on the service life of a Ti-supported IrO2 electrode was studied in mixed aqueous solutions of H2SO4, (NH4)2SO4 and NH4F. The service life was prolonged by heat treating the Ti substrate prior to coating with IrO2. This was attributed to the increase in thickness of the TiO2 layer at the Ti/IrO2 interface.

PHOTOCONVERSION

Possible Ways and Prospects for Photocatalytic Conversion of Solar Energy
A comprehensive review is given of the various ways of photocatalytic conversion of solar energy. The main emphasis is on the chemical route involving photocatalytic decomposition of H2O to H2 and O2 in the presence of platinum group metals and other catalysts. (408 Refs.)

Photocatalytic Hydrogen Production from Liquid Methanol and Water
H2 was highly efficiently produced at room temperature from liquid MeOH and H2O using a TiO2 powder photocatalyst mixed with Pt and Pd metal, RuO2 or [(Ph3P)3RhCl], irradiated by Xe.

Photocatalytic and Photoelectrochemical Hydrogen Production on Strontium Titanate Single Crystals
Sustained photogeneration of H2 was observed on platinised and metal SrTiO3 single crystals illuminated in aqueous alkaline electrolytes or in the presence of electrolyte films. H2 evolution increased with electrolyte hydroxide concentration. Platinised crystals appear to evolve H2 photoelectrochemically.

Cyclic Water Cleavage by Visible Light; Drastic Improvement of Yield of H2 and O2 with Bifunctional Redox Catalysts
A new catalyst promotes both H2O and O2 formation in the Ru(bpy)32+/methyl viologen system. This catalyst consists of RuO2 (0.1%) in (Nb-doped) n-TiO2 charged with finely divided Pt. The rate of generation of H2 remains constant even after irradiation for 4 days in visible light.
ELECTRODEPOSITION AND SURFACE COATINGS

Improvement of Ti Alloy Fatigue Properties by Pt Ion Plating
The effect of Pt ion plating on the high cycle axial fatigue life of Ti-6Al-2Sn-4Zr-2Mo specimens was studied at room temperature and 455°C. Plated specimens had increased fatigue strength, greater at 455°C than room temperature. Coated specimens cycled close to the fatigue limit at 455°C had the highest improvement, associated with subsurface fatigue crack initiation. Uncoated specimens failed by surface cracking. Pt ion plating caused surface hardening and oxidation resistance at elevated temperatures, suppressing surface crack initiation.

R.F. Magnetron Sputtering of Thick Platinum Coatings in Glass Microspheres
Thick Pt coatings on glass microspheres are needed for proposed laser fusion targets. The spherical nature of these substrates, combined with the small dimensions makes it difficult to achieve a smooth and uniform coating. An ultrasonic vibrating screened cage and a r.f. magnetron sputter gun were used to batch coat microspheres successfully with up to 6 μm of Pt, with a surface roughness of 200 nm, a thickness non-concentricity of 300 nm and a density > 98% of the bulk Pt density.

Hydrous Melt Catalyst Synthesis
A new way to prepare Sn-Pd electroless plating catalysts using hydrated melts is described. Pure stannous chloride melts rapidly reduce Pd halides to a noncatalytic state. Adding alkali halides greatly modifies this reaction to give stable catalytic species. The solidified melt dissolves readily in dilute HCl. This solution is highly active as a catalyst for electroless plating of nonconductors.

HETEROGENEOUS CATALYSIS

The Combustion of Methane on Platinum-Alumina Fibre Catalysts. II. Design and Testing of a Convective-Diffusive Type Catalytic Combustor
A convective-diffusive catalytic combustor was used to study the total oxidation of CH4 over a Pt/Al2O3 fibre catalyst. Temperature profiles across the catalyst pad were measured as a function of CH4 feed rate, as were the radiant energy and the gas composition near the pad. CO and H2O were the only detectable products of the reaction.

Solid State Reactions in Catalysts and Components of Catalysts. VI. Studies on Pt/γ-Al2O3 Catalysts Modified by Chlorine
The effect of tri- and tetrachloromethanes on the solid state behaviour of 0.98wt.%Pt/γ-Al2O3 catalysts was studied in an oxidising atmosphere. The total Cl content, CO chemisorption capacity and content of oxidized Pt were determined. The treatment of the catalysts with tri- and tetrachloromethanes greatly affected the above parameters, and also the catalytic properties of the catalysts during hydrocarbon conversion reactions.

Deactivation of a Catalyst in a Tubular Reactor in a Strongly Exothermic Reaction. II. Experimental Study of the Occurrence of Multiple Stationary States and Parametric Sensitivity
The effect of deactivation of an industrial Pt/Al2O3 catalyst on the parametric sensitivity and on the multiple stationary states was studied during co-oxidation in a tubular, non-isothermal reactor. The catalyst was found to be deactivated by tetraethyl Pb and deactivation strongly affected the parametric sensitivity and the occurrence of multiple stationary states; the latter occurs during the first stages at the lower input temperature.

Heterogeneous-Catalytic Decomposition of H2O2 on Pt/Pt in Solution of Chlorohydrin Styrene Solution
Heterogeneous catalytic decomposition of H2O2 on Pt/Pt in the presence of chlorohydrin styrene (CHS) showed the formation of various intermediate products yielding various industrial styrenes. In the heterogeneous catalytic system Pt/Pt-H2O2-CHS, the homogeneous oxidation process leads to the accumulation of difficult to oxidise intermediate products. Their adsorption on the catalysts inhibits the heterogeneous decomposition of H2O2 and thus also the additional oxidation of the decomposition products.

A review is given of SiO2 carriers from the viewpoint of texture, structure and surface chemistry. The effects of carrier properties on activity and selectivity of Pt/SiO2 and MoO3/SiO2 and WO3/SiO2 as active components in the conversion of hydrocarbons are discussed. (43 Refs.)
Effect of Faujasite Type Carrier on the Activity of Platinum Supported Catalysts in Toluene Hydrogenation


A comparative study of the hydrogenation of toluene to methylcyclohexane at 25°C on Pt/Y zeolite and Pd/SiO₂ catalysts showed that the catalytic activity of Pt/zeolite was higher than Pt/SiO₂ catalysts of the same metal surface area. Faujasite type zeolites adsorb irreversibly a large amount of toluene which is rapidly converted into methylcyclohexane on contact with H₂ at room temperature. The toluene is activated when adsorbed on Y zeolites, whereas on Pt/SiO₂, the reaction only takes place between H₂ and toluene both adsorbed on Pt.

Physico-Chemical Study of Platinum-Chromium/Alumina Catalysts


Physico-chemical study of Pt-Cr/Al₂O₃ catalysts containing 0.4 wt.% Pt and 0.05–5 wt.% Cr was performed spectroscopically and by the static magnetic susceptibility method during calcination and reduction. The catalytic effect of Pt on the reduction of Cr in the catalyst was observed; Cr was reduced and compounds of Pt and Cr were formed.

Study of Platinum-Lithium-Alumina Catalysts in the Processes of n-Decane Dehydrogenation by Means of Impulse Method


The effect of the addition of up to 2.5 wt.% Li on the catalytic properties of 0.5 wt.% Pt-Li/Al₂O₃ catalysts was studied during n-decane dehydrogenation by the impulse technique. The catalysts containing 2.5 wt.% Li were 3 times less acidic at 200–450°C, and a decrease in the number of weak and medium acid centres was observed in 0.1 wt.% Li and of strongly acidic centres in >1 wt.% Li containing catalysts. The addition of Li to the catalysts increased the monolefin content in the reaction yield. The reaction was highly selective in the presence of Pt-1 wt.% Li/Al₂O₃ catalysts.

Hydrogenation of Dihydrolinalool into Linalool on Pd/Al₂O₃ Catalysts


Studies were made of hydrogenation of dihydrolinalool on Pd/Al₂O₃ catalysts, containing 0.5, 2.0 or 5% Pd, in the presence of alcohols C₃–C₅ of various compositions. The 0.5% Pd/Al₂O₃ catalyst with highly homogeneous particles and the highest dispersity showed the maximum selectivity.

Metal Support Interactions in the Palladium-Catalysed Decomposition of Furfural to Furan


The catalysed decarbonylation of furfural to furan by Pd/C and Pd/Al₂O₃ was examined. There was a combination of support effects which are possibly related to a direct electronic support function whereby furfural and H can be adsorbed on support surfaces with subsequent surface migration to metal sites for the reaction. Pd/C may be better than Pd/Al₂O₃ because of its ability to modify the electronic nature of Pd and also its absorptive characteristics.

Ethylene Oligomerisation on Pd/Alumosilicate Catalysts under Pressure


Studies of the conversion of C₂H₄ on 3% Pd/alumosilicate (zeolite), 2% Pd/CaNAX and 0.1% Pd%/CaNaY saturated catalysts under a pressure of 5–20 atm showed that at 100°C Pd/alumosilicate and Pd/CaNAX catalysts go through the maximum at 10–15 atm with a rate of conversion for C₂H₄ of 15–20%. Saturated Pd/alumosilicate catalysts under pressure were highly selective during the dimerisation of C₂H₄. The yield of butenes of the reacted C₂H₄ reached 93.5%.

HOMOGENEOUS CATALYSIS

Combined Actions of Enzyme and Metal Catalyst, Applied to the Preparation of D-Mannitol


A novel catalytic approach involving co-operation of a bio- and a chemo-catalyst was applied in the simultaneous enzymatic interconversion and Pt metal-catalysed hydrogenation of D-fructose-D-glucose mixture, (water, pH 7–8, 60°C and 20 atm H₂). This gives an enhanced yield of D-mannitol.

Precursor of an Extraordinarily Reactive Homogeneous Hydrogenation Catalyst, Synthesis, X-Ray Crystal Structure, and Reactions of [closo-1,3-µ-(η-3,4-CH₂CH₂CH₂)-3-H-3-PPh₃,1,2-Rh₂C₂B₁₀H₁₀]


The synthesis, X-ray crystal structure and reactions of the title catalyst precursor are given. The complex is the most active homogeneous hydrogenation catalyst so far reported and is probably the first Rh complex of the rare hydrido-alkene class of complexes to be isolated and characterised.
Homogeneous Catalytic Hydrogenation of Carboxylic Acid Esters to Alcohols
The homogeneous catalytic hydrogenation of activated and simple aliphatic carboxylic acid esters to their corresponding primary alcohols has been accomplished under mild conditions, 90°C, 620 kPa of H₂, using a novel anionic Ru hydride complex.

ELECTRICAL AND ELECTRONIC ENGINEERING
Platinum-Induced Hysteresis and Non-volatile Memory Properties in MOS Systems (PLATMOS)
Pt was diffused into MOS p-type Si <111> and <100> oriented structures of 3–5Ω cm resistivity and was studied by h.f. capacitance/voltage techniques. The Pt produced hysteresis in the MOS system which has not been previously observed. The hysteresis depends strongly on diffusion time and crystal orientation, being more pronounced in <111> wafers than <100>. This observation is associated with some bias-dependent charge storage at the oxide/Si interface or mobile Pt ions in the oxide. This hysteresis could be used as a memory element due to being nonvolatile.

NEW PATENTS
ELECTROCHEMISTRY
Platinum Coated Gas Turbine Igniters
JOHNSON MATTHEY & CO. LTD. British Patent 1,572,339
Electrode erosion and/or corrosion is avoided when the electrode working surfaces of the ignitor are made from a host material in which Co, Ni and/or W predominates and is alloyed with one or more platinum group metals (except Os).

ELECTRODEPOSITION AND SURFACE COATINGS
Palladium Chemical Plating Bath
MINE SAFETY APPLIANCES CO British Appl. 2,040,316 A
A bath for the chemical (electroless) deposition of Pd contains a divalent Pd salt, NH₄, or an amine and a tertiary amine borane, optionally with an organic stabiliser. A hard Pd alloy film is obtained containing 1–5% each of amorphous B and PdH₁₋₂. The substrate is preferably Ni.

Shallow Silicide Contacts Formed by Using Codeposited Pt₂Si and Pt₁₂Si Films
Shallow silicide contacts were made on Si by using co-deposited Pt₂Si and Pt₁₂Si alloyed films. Cross-sectional TEM showed that a uniform contact 10 nm deep was achieved by both films. Current-voltage measurements showed that the Schottky barrier height of these shallow contacts was as good as that of PtSi made by reacting pure Pt with n-Si.

Platinum Group Metal Thermal Barriers
JOHNSON MATTHEY & CO. LTD. British Appl. 2,041,246 A
Coatings on Ni, Co or Fe-based superalloys, refractory alloys or refractory metals include a protective layer of one or more platinum group metal and a refractory metal oxide such as Al₂O₃, ZnO, TiO₂.

Activating Polymeric Substrates Prior to Electroless Plating
OXY METAL INDUSTRIES CORP. U.S. Patent 4,204,013
An accelerating solution containing substituted alkyl amine, is used on polymeric substrates activated with acidic Sn-Pd complexes to provide total metal coverage by subsequent electroless plating.

Platinum Plating
A. G. KOZLOV and N. A. NEROZIN Russian Patent 732,412
For plating Ti, the bath preferably contains 15 g/l Pt as a Pt diaminodinitrite, 100 g/l NH₄NO₃, 10 g/l NaNO₂, NH₂ to pH 7.5, and the reaction is carried out at a current density of 5–12A/dm² and 70–80°C.