

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Diffusion in Thin Film Couples of Platinum-Gold

W. B. NOWAK and R. N. DYER, *J. Vacuum Sci. Technol.*, 1972, 9, (1), 279-283

The interdiffusion of Pt and Au films was studied up to 550°C. Diffusion was monitored by plotting spectral reflectance against wavelength in the band 500-100 nm. Analysis of Pt diffusion through Au films gave an activation energy of ~38 kcal/g-atom and a pre-exponential factor of the order 10^{-3} cm²/s, values close to those for volume diffusion. Results have particular relevance to microcircuit beam-lead technology.

The Low Temperature Electrical Resistivity and Thermoelectric Power of Palladium-Platinum Alloys

P. BLOOD and D. GREIG, *J. Phys. F: Metal Phys.*, 1972, 2, (1), 79-88

The electrical resistivity and thermoelectric power of Pd-Pt alloys were measured as a function of temperature at 1-100K. The low temperature thermopowers at the two ends of the alloy series have opposite signs.

Significance of Electric Fields on the Growth of Thin Metal Films

L. E. MURR and H. P. SINGH, *Appl. Phys. Lett.*, 1972, 20, (12), 512-514

Pt and Pd thin films were vapour-deposited on to air-cleaved NaCl (001) substrates in the absence of an electric field and in the presence of d.c. fields in the plane of the substrate of 10-10³V/cm. No significant effects of this field were apparent on examination of samples of the evaporated films.

High-temperature Transport Properties of Palladium

M. J. LAUBITZ and T. MATSUMURA, *Can. J. Phys.*, 1972, 50, (3), 196-205

The thermal conductivity, electrical resistivity and absolute thermoelectric power of pure Pd were determined at 90-1300K. Results are compared with existing data and are analysed in terms of a simple two-band model, where one band contains the carriers and the other acts as a trap into which phonons scatter the carriers.

Desorption of Hydrogen from Palladium and Palladium-Silver Alloys followed by Differential Scanning Calorimetry

D. ARTMAN and T. B. FLANAGAN, *Can. J. Chem.*, 1972, 50, (9), 1321-1324

Differential scanning calorimetric curves were

obtained corresponding to the desorption of H₂ from Pd and Pd-Ag alloys. The heat of desorption was measured. Solid-state diffusion is not the limiting step for palladised Ag-Pd but may be for unpalladised Ag-Pd.

On the Oxidation of Palladium, Silver, Silver-Palladium, and Silver-Palladium-Copper Alloys

U. HARMSEN and W. MERL, *Metall.*, 1972, 26, (7), 680-682

The transition resistance of Pd, Ag, 30%Pd-Ag, 50%Pd-Ag, and 5%Cu-25%Pd-Ag was measured using a fully automatic apparatus. The contact resistance increases in the region of the stable PdO layer, but falls to its initial value at 800°C when the PdO evaporates. The alloy 5%Cu-25%Pd-Ag has a higher transition resistance owing to the oxidation of Cu above 800°C.

Ordered Alloys in the Cobalt-Palladium System

Y. MATSUO, *J. Phys. Soc. Japan*, 1972, 32, (4), 972-978

Ordered phases on the 20-100 at.%Pd-Co alloy system were studied by electron diffraction using evaporated single crystal films. Two types of ordered state were found; one is of L1₂ type (Cu₃Au type) and exists in 60-90 at.%Pd. For 80 at.%Pd-Co the order-disorder transition occurs at 830°C. The other has the L1₀ type structure (CuAuI type) and exists in a narrow composition range around the equiatomic alloy. This phase is accompanied by two phase regions over wide composition ranges both sides of 50 at.% Pd-Co.

Constitution Diagram of the Titanium-Palladium System

V. N. EREMENKO and T. D. SHTEPA, *Porosh. Metall.*, 1972, (3), 75-81

The Pd-Ti system was investigated by X-ray, metallographic and differential thermal analyses over the whole concentration range, and the phase diagram is given. Pd forms the intermediate phases Ti₄Pd, Ti₂Pd, TiPd, TiPd₃ and TiPd₃. The Ti₄Pd phase is formed at ~600°C; the TiPd₃ phase is due to ordering of the β-solid solution; the TiPd phase melts congruently and the TiPd₃ phase appears in peritectic reaction at 1400°C.

The Deformation of Amorphous Palladium-20 at.% Silicon

R. MADDIN and T. MASUMOTO, *Mater. Sci. Engng.*, 1972, 9, (3), 153-162

The time-dependent mechanical properties of

amorphous 20 at.% Si-Pd, i.e. fracture-strain rate effect, load relaxation, creep and elastic after-effect characteristics, were measured as a function of stress and temperature. The viscous nature of the amorphous phase is explained, and a qualitative model for the change from the amorphous to the crystalline phase is suggested.

The Hf-Pd Constitution Diagram

A. K. SHURIN and V. V. PET'KOV, *Izv. Akad. Nauk S.S.S.R., Metall.*, 1972, (2), 166-168

Studies of the Hf-Pd system showed that Pd lowers the melting point of Hf with the formation of an eutectic and also lowers the temperature of allotropic conversion with the formation of an eutectoid. The structures of Hf_2Pd , HfPd_2 and HfPd_3 were confirmed. HfPd and Hf_3Pd_4 (Hf_2Pd_3) were detected. There were no laves phases. Solubility of Hf in Pd is up to 22.5 at.% but of Pd in Hf is only up to 1 at.% in α -Hf and <5at.% in β -Hf.

Equiatomic Transition Metal Alloys of Manganese. VIII. Structural and Magnetic Properties of Rh-Mn Phases

K. SELTE, E. BJERKELUND, A. KJEKSHUS, A. F. ANDRESEN, W. B. PEARSON and V. MEISALO, *Acta Chem. Scand.*, 1972, 26, (2), 719-732

The structural and magnetic properties of 44-72 at.% Mn-Rh were studied. The cubic RhMn phase with CsCl-type structure is stable at higher temperatures and 50-58 at.% Mn. It has not been obtained in an ordered magnetic state. It transforms on cooling to a tetragonal phase with CuAu(I) type structure; this is in an antiferromagnetically ordered state.

Some Structural and Physical Properties of 'As Cast' Molybdenum-Ruthenium Alloys

P. E. J. FLEWITT and A. J. TATE, *J. Less-common Metals*, 1972, 27, (3), 339-352

The microstructure, hardness and superconducting transition temperature of high purity 'as cast' 10-45% Ru-Mo alloys are reported. The morphology and crystallography of the three phases (α , β , σ) which occur singly or in combination within this composition range were analysed using optical and electron microscopy.

Alloys of Thorium with Certain Transition Metals. V. The ThO_2 - ThIr_2 Pseudo-binary System and Some Additional Results on the Thorium-Iridium System

J. R. THOMSON, *J. Less-common Metals*, 1972, 27, (3), 293-296

The ThO_2 - ThIr_2 pseudo-binary system was studied using X-ray and metallographic methods. The composition range of stability of the cubic CI5 -type phase was investigated and information was obtained on the stability of other phases. Metallographic results on binary 66-83 wt.% Ir-In are reported.

CHEMICAL COMPOUNDS

Electronic Energy Bands of Metal Hydrides - Palladium and Nickel Hydride

A. C. SWITENDICK, *Ber. Bunsenges. Phys. Chem.*, 1972, 76, (6), 635-643

Energy band calculations for the Pd-H system were carried out with the H atoms occupying interstitial positions in the f.c.c. Pd lattice to represent PdH_x with $x=0.25, 0.75, 1.0$ and 2.0 . The calculations show why β -phase PdH saturates at higher H concentrations than the known concentration of holes in Pd d bands.

Conduction Mechanism in Square Planar Complexes of Platinum

P. WURFEL, H. D. HAUSEN, K. KROGMANN and P. STAMPFL, *Phys. Status Solidi A*, 1972, 10, (2), 537-541

A strong dependence of conductivity upon lattice distortions and humidity was detected in square planar complexes of Pt. Both electronic conduction and ionic conduction were found. Observed results are probably related to the influence of humidity on electronic conductivity.

Confirmation of One Dimensional Metallic Behaviour in $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}(\text{H}_2\text{O})_n$ by Far Infrared Reflection

P. BRÜESCH and F. LEHMANN, *Solid State Commun.*, 1972, 10, (6), 579-580

Far infrared reflection measurements on single crystals of $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}(\text{H}_2\text{O})_n$ show an unusually high anisotropy of the reflectivity and confirm the almost one dimensional metallic behaviour of this compound.

Suppression of Graft-versus-Host Reaction by *cis*-Platinum(II) Diamminodichloride

A. KHAN and J. M. HILL, *Transplantation*, 1972, 13, (1), 55-57

The antitumour agent *cis*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ (5-10 mg/kg, i.p.) decreased the graft-versus-host reaction in B6AF₁ mice.

Hydride Complexes of the Transition Metals

H. D. KAESZ and R. B. SAILLANT, *Chem. Rev.*, 1972, 72, (3), 231-281

Hydride complexes of transition metals including the Pt metals are reviewed. Methods of synthesis and properties and reactions are discussed together with spectroscopic characteristics and structure determinations.

ELECTROCHEMISTRY

True Temperature Coefficients of the Electric Tension of Individual Electrodes. X. The Pt- H_2/H^+ Electrode

G. MILAZZO and V. K. SHARMA, *Z. Phys. Chem. (Frankfurt)*, 1972, 79, (1-2), 41-61

The non-isothermal temperature coefficient of

the Pt-H₂/H⁺ electrode was measured in aqueous HCl. The temperature coefficients are 859.6 at 25°C and 884.0 at 35°C.

ELECTRODEPOSITION AND SURFACE COATINGS

Deposition of Platinum by Chemical Reduction of Aqueous Solutions

F. H. LEAMAN, *Plating*, 1972, **59**, (5), 440-444

The most successful chemical plating processes which have been developed for depositing dense, adherent layers of Pt on to noble metals and alloys and on catalysed nonconductive substrates are described. Various applications of these processes and the advantages and disadvantages of each are outlined.

Precious-metal Coatings for the Protection of Refractory Metals

B. JONES, M. W. JONES and D. W. RHYS, *J. Inst. Metals*, 1972, **100**, (5), 136-141

The use of Pt-Au and Pd-Au coatings for protection from oxidation of Ir, Ru, W and Mo was studied. The compatibility of the alloys was assessed from the phase equilibria and direction of the lines in the ternary systems of Pt-Au and Pd-Au with the four refractory metals. Pt-Au can be used to protect only Pt-rich Pt-Ru alloys; Pt-Au is suitable for unalloyed refractory metals. Pd-Au has a tendency to diffuse O, but could be used for interdiffusion barriers between refractory metals and oxidation resistant coatings.

Reduction of Pd(II) with Sn(II) in Hydrochloric Acid. Studies on the Metallisation of Plastics. Part I

M. TSUKAHARA, T. KISHI, H. YAMAMOTO and T. NAGAI, *J. Metal Finish. Soc. Japan*, 1972, **23**, (2), 83-89

The reduction of Pd(II) with Sn(II) in HCl solution was investigated by potentiometric, spectrophotometric and polarographic methods. [Pd(II)Sn(II)_mCl_x]ⁿ⁻ ions (m=2 or 6) were formed during the process and gradually decomposed to form free Pd(0) and Sn(IV). The negatively charged Pd colloid - stabilised by adsorption of Sn(II) - was assumed to act as an active site in the electroless plating process.

HETEROGENEOUS CATALYSIS

Reaction of Nitric Oxide with Hydrogen on Platinum Purified in Ultra-high Vacuum

I. I. TRET'YAKOV, V. N. KORCHAK and B. R. SHUB, *Kinet. Kataliz*, 1972, **13**, (2), 512-514

H₂ reacts with NO on Pt purified in ultra-high vacuum to form either N₂ or NH₃. The selectivity of the process depends on both catalyst temperature and the partial pressures of the gases. A

mechanism is proposed for N₂ and NH₃ formation by way of intermediate products with adsorbed N atoms.

Catalytic Decomposition of Nitrogen Dioxide on a Heated Platinum Wire

B. G. ONG and D. M. MASON, *Ind. Engng. Chem., Fund.*, 1972, **11**, (2), 169-174

In the study of natural convection heat transfer from a Pt wire to the endothermically reacting gaseous system 2NO₂ ⇌ 2NO + O₂, a large increase in the heat flux is observed at a wire temperature ~1100K at 0.2-1 atm. This is probably because below 1100K the wire is coated with PtO₂. Above 1100K the oxide decomposes to pure Pt which catalyses the NO₂ decomposition and causes an increase in heat flux.

Modelling and Optimisation of the Ammonia Oxidation Process for Nitric Acid Manufacture

P. URONEN and F. KIUKANNIEM, *Br. Chem. Engng. Process Technol.*, 1972, **17**, (4), 323-325

A semi-empirical mathematical model for the oxidation of NH₃ over 5-10% Rh-Pt catalyst was derived. A simulation study was carried out and the effect of feed temperature, NH₃ content of feed, total gas charge and number and dimensions of sieves has been studied.

Catalyst Aids Selective Hydrogenation of Acetylene

W. K. LAM and L. LLOYD, *Oil Gas J.*, 1972, **70**, (13, Mar. 27), 66-70

0.04 wt.% Pt/α-Al₂O₃, developed by ICI under the name 38-1, is used for the selective hydrogenation of C₂H₂ to C₂H₄ and C₃H₆. Catalyst formulation and reactor design, operating temperature and catalyst performance are discussed.

Chemisorption on Supported Platinum. I. Evaluation of a Pulse Method. II. Stoichiometry for Hydrogen, Oxygen and Carbon Monoxide

J. FREEL, *J. Catalysis*, 1972, **25**, (1), 139-148, 149-160

A flow method was used to measure H₂ chemisorption on Pt/Al₂O₃ and Pt/SiO₂. The results agreed with those obtained using static methods at room temperature. At 200-300°C a substantial volume of H₂ was reversibly chemisorbed which was excluded from the flow determination.

Dehydrocyclisation of 1-Ethyl-naphthalene and Hydrogenolysis of Acenaphthene in the Presence of Pt-C

L. A. ERIVANSKAYA, A. KHALIMA-MANSUR, YU. K. GRISHIN and A. F. PLATE, *Neftekhimiya*, 1972, **12**, (2), 183-187

1-Ethyl-naphthalene undergoes dehydrocyclisation at 310-420°C over Pt/C to acenaphthene. Hydro-

genolysis of the latter forms naphthalene-1, 1-methyl- and 1-ethylnaphthalenes. Below 390°C the active surface of the catalyst is poisoned as dehydrocyclisation of ethylnaphthalene and hydrogenolysis of acenaphthene occur.

Preparation of a Well Dispersed Platinum-Iron Alloy on Carbon

C. H. BARTHOLOMEW and M. BOUDART, *J. Catalysis*, 1971, **25**, (1), 173-176

A method for the preparation of Pt-Fe alloy catalyst with average particles 30-40Å in diameter supported on graphitised C is described. The method consists of four steps: partial oxidation of the support, impregnation with H_2PtCl_6 and $Fe(NO_3)_3$ in 4 : 1 C_6H_6 - C_2H_5OH mixture, drying the impregnated samples, and reduction at 500°C in H_2 .

Hydrogenation of Ethylenes on Supported Platinum

J. C. SCHLATTER and M. BOUDART, *J. Catalysis*, 1972, **24**, (3), 482-492

The rate of hydrogenation of C_2H_4 on Pt/SiO₂ was studied at 207-371 K. The results agree with those of others on films of evaporated Pt. Enhanced activity was observed when Pt/SiO₂- γ -Al₂O₃ was used. There was no evidence for correlating spillover of H₂ from the metal to the Al₂O₃ with enhanced rates of hydrogenation of C_2H_4 adsorbed on the Al₂O₃.

Selective Hydrogenolysis of Methylcyclopropane over Bifunctional Catalysts

J. C. SCHLATTER and M. BOUDART, *J. Catalysis*, 1972, **25**, (1), 93-98

Hydrogenation of methylcyclopropane proceeds at different rates to yield *iso*-C₄H₁₀ or *n*-C₄H₁₀. The ratio of these rates at 0°C (selectivity) was studied on Pt/silica gel. The selectivity was ~20 when the catalyst was used alone or with excess silica gel. When mixed with Al₂O₃ or silica gel diluents, selectivity dropped to ~0.1. This is probably due to isomerisation on the diluent to *n*-C₄H₁₀, followed by hydrogenation to *n*-C₄H₁₀ on the metal.

The Anodic Oxidation of Hydrogen on Platinised Tungsten Oxides. I. Composition of Tungsten Blue in Platinised WO₃ Hydrogen Electrocatalyst

B. S. HOBBS and A. C. C. TSEUNG, *J. Electrochem. Soc.*, 1972, **119**, (5), 580-583

The mechanism of the synergistic effect using Pt/WO₃ catalysts in H₂ electrodes depends on the composition and mode of formation of a reduced intermediate W oxide. Chemical analysis and X-ray diffraction show it to consist of blue bronze. Mechanical mixtures and impregnated powders were investigated at different temperatures, Pt loadings and pH values. The greatest reduction (H_{0.44}WO₃) was obtained using WO₃

impregnated with 0.8 wt.% Pt in acidic solution at 25°C.

Activity of Hydrogenation Catalysts in an Ultrasonic Field

I. V. SOLOV'EVA and A. N. MAL'TSEV, *Zh. Fiz. Khim.*, 1972, **46**, (5), 1332-1333

Studies of the hydrogenation of acrylic acid revealed that an ultrasonic field doubled the activity of Pt black and more than trebled that of Pd black. At 15-35°C the activation energies of Pt and Pd were 3.0 and 2.5 kcal/mole respectively.

Characterisation of Palladium Blacks. I. A Novel Hydrogen Pretreatment and Surface Area Determination of Palladium

P. A. SERMON, *J. Catalysis*, 1972, **24**, (3), 460-466

A method for the determination of Pd surface areas using H₂ chemisorption is described. The results obtained for a series of Pd blacks covering a wide range of surface areas are given. The method is independent of the extent to which O₂ is preadsorbed on the metal surface.

II. Comparison of Various Methods of Estimating Surface Area or Particle Size

P. A. SERMON, *J. Catalysis*, 1972, **24**, (3), 467-471

Series of Pd blacks of widely differing surface area were characterised by techniques including N₂ and Kr adsorption, H₂ chemisorption, electron microscopy, and X-ray diffraction. The precision of these techniques is estimated from a comparison of the results.

Carbon-supported Platinum Metal Catalysts for Hydrogenation Reactions. Mass Transport Effects in Liquid Phase Hydrogenation over Pd/C

G. J. K. ACRES and B. J. COOPER, *J. Appl. Chem. Biotechnol.*, 1972, **22**, (6), 769-785

The efficient use of Pd/C catalysts in liquid phase hydrogenation is shown to depend on H transport limitations from the bulk liquid to catalyst particles and on H₂ diffusion through the support to the active crystallites. These processes limit the maximum hydrogenation rate and affect the selectivity. Factors controlling output are examined.

Effect of the Nature of the Solvent on the Kinetics of Hydrogenation of Dimethylethylnylcarbinol on Palladium/Polyacrylonitrile Catalyst by Reduction in Optimum Conditions

O. A. TYURENKOVA, L. A. CHIMAROVA and F. I. ALEKSANDROVA, *Zh. Fiz. Khim.*, 1972, **46**, (4), 885-889

The hydrogenation of dimethylethylnylcarbinol over Pd/polyacrylonitrile was studied in *iso*-amyl alcohol, in H₂O, in H₂O-alcohol, in H₂O-acetone, and also in acid and alkaline media.

Adsorption Properties of Rhodium-Ruthenium Catalysts in Relation to Hydrogen

T. I. KIM, T. M. GRISHINA and G. D. VOVCHEKNO, *Zh. Fiz. Khim.*, 1972, **46**, (4), 960-962

The adsorption capacity of Rh-Ru alloys increases as the content of Ru increases. Catalysts were prepared by CO-deposition from salt solutions. Studies were by charging curves.

Investigation of the Kinetics of the Catalytic Dealkylation of Toluene

L. N. GRIGOR'eva, G. N. MASLYANSKII, G. L. RABINOVICH and T. A. SLOVOKHOTOVA, *Neftekhimiya*, 1972, **12**, (2), 195-199

Studies of the conversion of toluene with H₂O vapour over 0.6% Rh/Al₂O₃ at 440-480°C showed dealkylation of toluene and the formation of gaseous products to complete the conversion. The rate of demethylation is proportional to the amount of toluene present. The rate of CH₄ accumulation correlates with the rate of complete breakdown of the toluene.

Some Problems of the Kinetics and Mechanism of Hydrogenolysis of Cyclopentane Hydrocarbons on Rhodium/Carbon

O. V. BRAGIN, T. G. OLFER'eva and A. L. LIBERMAN, *Kinet. Kataliz*, 1972, **13**, (2), 380-384

The selectivity of hydrogenolysis of *trans*-1,2-dimethyl- and ethylcyclopentane over 20% Rh/C is considerably displaced towards the unshielded bonds compared with hydrogenolysis over Pt/C. The apparent activation energy over Rh/C for hydrogenolysis of *trans*-1,2-dimethylcyclopentane is 24 kcal/mole; for ethylcyclopentane it is 18 kcal/mole. These results broadly agree with the ribbed doublet mechanism of cyclane hydrogenolysis.

Dehydrocyclisation of 2-*n*-Butylnaphthalene in the Presence of Rhodium-Alumina Catalyst

L. A. ERIVANSKAYA, G. A. SHEVTSOVA and A. F. PLATE, *Neftekhimiya*, 1972, **12**, (3), 329-333

2-*n*-Butylnaphthalene at 370-560°C in the presence of 0.5 wt. % Rh/Al₂O₃ undergoes C₆-dehydrocyclisation to form mainly phenanthrene, C₅-dehydrocyclisation, dehydrogenation, and hydrogenolysis of alkyl groups. The latter reaction is predominant as successive terminal methyl groups are split off.

HOMOGENEOUS CATALYSIS

Linear Dimerisation and Codimerisation of 1,3,7-Octatriene

W. KEIM and H. CHUNG, *J. Org. Chem.*, 1972, **37**, (7), 947-950

The linear dimerisation of 1,3,7-octatriene using

bis- π -allylpalladium yields *n*-hexadecapentaenes in high selectivity. The same catalyst was active for the codimerisation of 1,3,7-octatriene with other polyolefins such as 1,3,6-heptatriene and 1,3,6-octatriene producing linear olefins in the C₁₆-C₂₄ range. The addition of phosphine ligands alters the course of the reaction and branched dimers are formed.

Noble Metal Catalysis. I. Synthesis of Succinates from Olefins

D. M. FENTON and P. J. STEINWAND, *J. Org. Chem.*, 1972, **37**, (12), 2034-2035

Dialkyl succinate yields of over 90% were achieved by the oxidative carbonylation of olefins in the presence of alcohols with a Pd redox system involving Fe and Cu chlorides. FeCl₂ in the presence of H⁺, was used, or CuCl added, to prevent the formation of HCl which slowed the reaction and decreased the yield. NaOAc and alkyl orthoformates increased the yield. The product distribution depended on the CO/olefin ratio.

Hydroformylation of Propene under Mild Conditions Using Rh₄(CO)₁₂

P. CHINI, S. MARTINENGO and G. GARLASCHELLI, *J. Chem. Soc., Chem. Commun.*, 1972, (12), 709-710

Stoichiometric amounts of H₂ and Rh₄(CO)₁₂ in toluene were used to catalyse the hydroformylation of C₃H₆. The reaction probably involves the dissociation of the catalyst. In polar solvents acyl derivatives were formed. Treatment of Rh₄(CO)₁₂ with a 1-2 fold excess of PPh₃ gave a phosphine complex which catalysed the hydroformylation of olefins.

Investigation of the Course and Mechanism of the Homogeneous Hydrogenation of Diene Hydrocarbons in the Presence of Tris(triphenylphosphine)chlororhodium

L. KH. FREIDLIN, E. F. LITVIN and L. F. TOPURIDZE, *Zh. Org. Khim.*, 1972, **8**, (4), 669-674

RhCl(PPh₃)₃ catalyses the reduction of C=C bonds in dienes successively and more selectively than does Rh black. The reduction of various butadienes is described.

Isomerisation of Bis Olefinic Acids with Rhodium Compounds

H. SINGER, W. STEIN and H. LEPPER, *Fette Seifen Anstrichmitt.*, 1972, **74**, (4), 193-198

The reaction mechanism and effect of catalyst composition and conditions were studied for the conjugation of isolated double bonds of bis-olefinic acids and esters by Rh compounds. RhCl(PPh₃)₃ and RhCOCl(PPh₃)₃ in the presence of SnCl₂·2H₂O were used to isomerise linoleic acid and its esters to conjugated *cis-trans* and *trans-trans* dienolic acids.

Investigation of Catalysis of Hydrogenation and Isomerisation of Pentenes by the Chlorodimethylsulphoxide Complex of Rhodium

L. KH. FREIDLIN, YU. A. KOPYTTSEV, N. M. NAZAROVA and T. I. VARAVA, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1972, (6), 1420

Reduced Rh chlorodimethylsulphoxide complexes catalyse homogeneous hydrogenation and isomerisation of pentenes at rates of conversion in the order: pentene-1 > 3-methylbutene-1 > *trans*-pentene-2 > *cis*-pentene-2. The reduction and isomerisation of 2-methylbutene-2 are probably prevented by steric problems. 2-Methylbutene-1 is not hydrogenated; it deactivates Rh catalysts for the conversion of olefins. Rh complexes do not catalyse reduction of dimethylsulphoxide by H₂ in the chosen conditions.

The Isomerisation of 1,4-Diarylbutenes by Ruthenium-Phosphine Complexes

J. BLUM and Y. BECKER, *J. Chem. Soc., Perkin Trans. II*, 1972, (8), 982-989

The catalytic double-bond migration in 1,4-diarylbutenes and in 2-methyl-1,4-diphenylbutenes by RuCl₂(PPh₃)₃ was studied. The electronic nature of the substituents does not affect the reaction rate but affects the ratio of the isomers formed. The reaction is sensitive to steric effects and to the electronic nature of the aryl ligands in the PPh₃ group of the catalyst.

Investigation of the Reduction of Cyclohexanones by Alcohols in the Presence of Tris(triphenylphosphine)dichlororuthenium

L. KH. FREIDLIN, V. Z. SHARF, V. N. KRUTII and S. I. SHCHERBAKOVA, *Zh. Org. Khim.*, 1972, 8, (5), 979-981

RuCl₂(PPh₃)₃ catalyses cyclohexanone reduction by addition of H from primary and secondary alcohols. The alcohols' reactivity depends on the number and structure of the hydrocarbon radicals at the carbonyl hydrocarbon atom.

Homogeneous Hydrogenation of Diene Hydrocarbons in the Presence of Triphenylphosphine Complexes of Ruthenium

E. F. LITVIN, L. KH. FREIDLIN and K. G. KARIMOV, *Neftekhimiya*, 1972, 12, (3), 318-323

In the presence of RuCl₂(PPh₃)₃ and of RuH(CF₃COO)(PPh₃)₃ diene hydrocarbons are hydrogenated with high selectivity and stereospecificity for the formation of *cis*-form β-olefins.

Dioxygen Complexes of Ruthenium as Homogeneous Catalysts for the Oxidation of Triphenylphosphine

B. W. GRAHAM, K. R. LAING, C. J. O'CONNOR and W. R. ROPER, *J. Chem. Soc., Dalton Trans.*, 1972, (12), 1237-1243

The complexes Ru(NCS)(CO)(NO)(PPh₃)₂ (I)

and Ru(O₂)(NCS)(NO)(PPh₃)₂ (II) are efficient catalysts for the oxidation of PPh₃ to OPPh₃. In xylene the rate was proportional to the catalyst concentration. The rate depends on the partial pressure of O₂ for (I) but not for (II). A mechanism is proposed.

FUEL CELLS

The Electrochemical Activity of Dispersed Platinum

K. F. BLURTON, P. GREENBERG, H. G. OSWIN and D. R. RUTTI, *J. Electrochem. Soc.*, 1972, 119, (5), 559-564

A highly dispersed Pt catalyst (Pt crystallite size less than 15 Å) on a conductive C support was prepared. These doped carbons were made into Teflon-bonded fuel cells electrodes and the Pt surface area and the dispersed Pt specific activity for O electroreduction in acid electrolyte were determined. The specific activity was ≈ 20 times less than that of crystalline Pt black. The lower activity may be due either to the difference in Pt crystallite sizes or to the support, or to both.

ELECTRICAL AND ELECTRONIC ENGINEERING

Conductive Ternary Oxides of Ruthenium, and Their Use in Thick Film Resistor Glazes

P. R. VAN LOAN, *Am. Ceram. Soc. Bull.*, 1972, 51, (3), 231-233, 242

Six ruthenites, CaRuO₃, SrRuO₃, BaRuO₃, Ti₂Ru₂O₇, Bi₂Ru₂O₇ and Pb₂Ru₂O₆, were investigated for use in thick-film resistive glazes for microelectronics. The first three have perovskite structures and the others have pyrochlore structures. They exhibit metallic conductivity, with resistivities of 10⁻²-10⁻⁴ ohm cm at room temperature, and excellent stability.

Reliability Studies on Ti-Pd-Au Metallisation

J. J. GELFAND and B. S. OU, *Extended Abstr.*, 141st Natl. Mtg., *Electrochem. Soc.*, 1972, 72-1, 67-68, abstr. 22

The resistivity of Ti-Pd-Au systems was measured and compared with Ti-Pt-Au systems. An investigation of the interaction of Pd with Au or Ti alone showed a greater resistance change for a thicker Pd interlayer. This indicates that Pd is not a barrier layer in the same sense as Pt. Diffusion of Pd into Au is the predominant mechanism for the observed resistance change.

Preparation, Structure and Electrical Properties of Thick Ruthenium Dioxide Films

S. PIZZINI, G. BUZZANCA, C. MARI, L. ROSSI and S. TORCHIO, *Mater. Res. Bull.*, 1972, 7, (5), 449-462

Results of measurements of X-ray diffraction, electron scanning microscopy and electrical

conductivity of thick, polycrystalline RuO_2 films obtained by decomposing RuCl_3 are presented and discussed. The influence of the preparation procedure, process temperature, Cl content and nature of substrate on the electrical and structural properties is also considered.

NEW PATENTS

METALS AND ALLOYS

Dispersion Strengthening of Metals

JOHNSON MATTHEY & CO. LTD.

British Patent 1,280,815

Platinum group metals are dispersion strengthened by spraying the metal or alloy with ~ 0.1 wt.% reactive metal, e.g. Zr, through an atmosphere which reacts preferentially with the reactive metal to form a dispersion strengthening material, e.g. ZrO_2 .

Dispersion Hardening of Pt Group Metals

JOHNSON MATTHEY & CO. LTD.

U.S. Patent 3,640,705

An oxidation resistant and high mechanical strength alloy is made by alloying a Pt group metal with an element capable of forming a stable refractory compound, and heating the alloy in a gas, e.g. air or O_2 , to form the refractory compound within the alloy. This corresponds to *British Patent 1,139,897*.

Treatment of Metals and Alloys

JOHNSON MATTHEY & CO. LTD.

German Offen. 1,533,481

The mechanical properties of metals, alloys and compounds are improved by cold working and annealing. Recrystallisation, which takes place during annealing, results in an elongated crystal or grain structure orientated in the direction of working.

ELECTRODEPOSITION AND SURFACE COATINGS

Plated Polymers

GULF & WESTERN INDUSTRIAL PRODUCTS CO.

British Patent 1,277,145

It has been found that in the electroless plating of polypropylene articles, much better results are obtained if $\text{Pd}(\text{NO}_3)_2$ rather than PdCl_2 is used as the activator.

Platinum Coatings on Cobalt Alloys

DEUTSCHE EDELSTAHLWERKE A.G.

British Patent 1,282,530

Turbine blades and other metal parts exposed to high temperatures are made from Co alloys

Fine Line Printing for Consumer Electronics

R. A. VOGEL, *Solid State Technol.*, 1972, 15, (5), 51-54

A system for printing Ag-Pd fine lines is described. Rheology and inks are discussed, together with printer characteristics and requirements.

coated with Pt group metals, e.g., Pt itself, optionally plated on over Ni.

Iridium Plating

INTERNATIONAL NICKEL CO. INC.

U.S. Patent 3,639,219

An Ir electroplating bath is prepared by digesting an aqueous solution of IrCl_3 and sulphamic acid at 100°C for an extended period, then adjusting the Ir content of the bath to about 3-20 g/l and adding about 3-20 g/l ammonium sulphamate.

LABORATORY APPARATUS AND TECHNIQUE

Palladium Alloy

DEUTSCHE GOLD- & SILBER-SCHNEIDANSTALT

German Offen. 2,043,492

Torsion strips in electrical meters are made from an alloy of Pd with 0.6-2% B.

HETEROGENEOUS CATALYSIS

Hydrogenation Catalyst

MARUZEN OIL CO.

British Patent 1,272,728

Selective hydrogenation of polyunsaturated hydrocarbons can be carried out in the presence of specified proportions of CO and a catalyst which is preferably supported, Cu-free Pd.

Hydrogenation Catalyst

F.M.C. CORP.

British Patent 1,273,280

In the production of H_2O_2 by the anthraquinone process, the hydrogenation catalyst is Pd metal supported on Al_2O_3 spheres of specified dimensions.

Hydrogenation Catalyst

B.P. CHEMICALS INTERNATIONAL LTD.

British Patent 1,273,874

12-Aminododecanoic acid (for use in the manufacture of nylon-12) is obtained by hydrogenation of 11-cyano-undecanoic acid in the presence of Ru metal deposited on a SiO_2 support.

Dehydrogenation Catalyst

V.E.B. LEUNA-WERKE 'WALTER ULBRICHT'

British Patent 1,275,830

Normal paraffins are dehydrogenated to linear