

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Epitaxial Growth and Structure of Evaporated Platinum Films on Rock Salt

J. KOSHY, *J. Crystal Growth*, 1976, **34**, (2), 345-349
Transmission electron microscopy was used to study the structure of Pt single crystal films 10-700Å thick, epitaxially grown by vacuum evaporation on the cubic, octahedral and dodecahedral planes of rock salt at 20-500°C. The Pt single crystals are shown to be in parallel orientation to the crystallographic planes in the substrate surface. Below a substrate temperature of 430-450°C the films were found to be polycrystalline, and became perfectly continuous at 600Å.

An Investigation of the Mechanism of the Oxidation of Carbon Monoxide Adsorbed onto a Smooth Pt Electrode in Aqueous Acid
C. MCCALLUM and D. PLETCHER, *J. Electroanal. Chem. Interfacial Electrochem.*, 1976, **70**, (3), 277-290

The mechanism of the anodic oxidation of CO adsorbed on to a smooth Pt surface was studied by potential step techniques. The heterogeneous chemical reaction between the adsorbed CO and the oxidised Pt species occurred at the edge of growth of two dimensional islands of the Pt oxide.

The Nature of Adsorption of some Simple Gases on Platinum

ZH. YA. SMORODINSKAYA, R. E. MARDALEISHVILI and D. MINK, *Dokl. Akad. Nauk S.S.S.R.*, 1976, **228**, (4), 900-903

Studies of the adsorption of N₂, Ar, O₂, CO and H₂O on a clean surface of Pt sponge and on the same surface covered with irreversibly adsorbed O₂ or CO were carried out by the determination of primary and secondary adsorption isotherms. The results show that the quantities of reversibly adsorbed Ar, N₂ and CO at -196°C and that of H₂O at 26°C on the surface of clean Pt are practically the same and coincide with the quantity of O₂ and H₂ adsorbed in the surface monolayer at 0 and -78°C.

Steric Properties of the Transition Metal Ions on Stepped Surfaces

Y. W. TSANG and L. M. FALICOV, *J. Phys. C, Solid State Phys.*, 1976, **9**, (1), 51-61

Studies of the effect of surface steps in the transition metals Pt and Au show that the steps definitely play a catalytic role in the case of Pt surfaces but do not increase the chemical reactivity of Au surfaces. The results are explained.

The Effect of Gold on Hydrogenolysis, Isomerisation and Dehydrocyclisation Reactions on Polycrystalline Platinum and Iridium Foils

D. I. HAGEN and G. A. SOMORJAI, *J. Catalysis*, 1976, **41**, (3), 466-481

Spectroscopic studies were made of the effect of the addition of Au to polycrystalline Pt and Ir foil samples on the initial reaction ratio for the hydrogenolysis, isomerisation and dehydrocyclisation reactions at 100-500°C and 10⁻⁴ torr. The results showed that the addition of Au to the Pt and Ir surfaces decreases the rates for all reactions studied. A linear decrease in isomerisation rate as a function of Au coverage was observed but hydrogenolysis and dehydrocyclisation decreased similarly, and more rapidly than isomerisation.

The Thermal Desorption of Carbon Monoxide from Platinum and Platinum-Gold Films

J. J. STEPHAN and V. PONEC, *J. Catalysis*, 1976, **42**, (1), 1-9

Studies of CO adsorption and desorption on Pt and Pt-Au films show that the amount of CO adsorbed on Pt-Au films at 295K and at pressure of 2 x 10⁻³ torr is low and almost independent of alloy composition. The thermal desorption spectrum of CO measured at 78-575K shows a broad peak caused by desorption from both Pt and Au. A broad maximum in the range 300-400K was also observed. A model for CO adsorption on Pt and Pt-Au films is proposed.

A New Platinum Fluoride: Pt^{II}Pt^{IV}F₆

A. TRESSAUD, F. PINTCHOVSKI, L. LOZANO, A. WOLD and P. HAGENMULLER, *Mater. Res. Bull.*, 1976, **11**, (6), 689-693

Studies of the Pt-F system show the existence of a new fluoride Pt^{II}Pt^{IV}F₆ which contains Pt in an oxidation state lower than that found in the already known Pt fluorides PtF₄, PtF₅ and PtF₆. The compound has a rhombohedral LiSbF₆-type structure with a=5.565Å and α=53.85°.

Plutonium-Palladium Pu₃Pd₅

D. T. CROMER, *Acta Cryst. B*, 1976, **32**, (6), 1930-1932

X-ray studies of a 67 at.% Pd-Pu alloy arc melted and heat treated at 950°C for 7 days showed the existence of a new compound Pu₃Pd₅ which crystallises in *Cmcm* space group with a=9.201, b=7.159, c=9.771Å, Z=4 and ρ_c=12.89 g/cm³. The new compound is thought to have the same structure as Ga₅Zr₃.

Effect of Fast Quenching on Phase Transformation and Structure of U-(0.05-6 at.%) Ru Alloys

A. A. ABOU-ZAHRA, F. H. HAMMAD and P. BOUDEAU, *J. Nucl. Mater.*, 1976, **60**, (1), 66-78

The structure of 0.05-6 at.% Ru-U alloys after fast quenching from the β and γ phases was studied using thermal analysis, X-ray diffraction, and optical and transmission electron microscopy. The results show that alloys containing 6, 3 and 1 at.% Ru, quenched from 900°C, transform martensitically to α -uranium. Uranium alloys containing 0.05 and 0.1 at.% Ru quenched from the β -phase show a fine α grain structure. This indicates that small amounts of Ru can be used for grain refining in U.

Ethylene Hydrogenation on Evaporated Iridium Films

P. MAHAFFY, P. B. MASTERSON and R. S. HANSEN, *J. Chem. Phys.*, 1976, **64**, (10), 3911-3916

Studies were made of the ethylene hydrogenation reaction catalysed by evaporated Ir thin films over a wide temperature range using isotope labelling techniques. The results showed that at 150K the rate of a surface dehydrogenation becomes significant. The microscopic surface area of the Ir films measured by H₂ adsorption is proportional to film thickness for average thicknesses of 30-200Å.

Thermal Dissociation of Iridium Dioxide

E. K. KAZENAS, V. K. TAGIROV, L. K. SHUBOCHKIN and D. M. CHIZHIKOV, *Zh. Neorg. Khim.*, 1976, **21**, (5), 1403-1404

A high temperature mass-spectrometric method was used to study the thermal dissociation of IrO₂ at 780-850K. It was found that the dissociation has a condensation character and is accompanied by a formation of solid solutions in the IrO₂-Ir system. The dissociation pressure and heat of dissociation of IrO₂ are given.

CHEMICAL COMPOUNDS

Chemistry of Metal Hydrides. XVII. Isocyanide Insertion into the Pt-H Bond, and the Formimidoyl Ligand. XVIII. The Formation of Secondary Carbene Complexes from Imidoyl Derivates

D. F. CHRISTIAN, H. C. CLARK and R. F. STEPANIAK, *J. Organometal. Chem.*, 1976, **112**, (2), 209-225, 227-241

The insertion of isocyanide into the Pt-H bond of the *trans*-[PtH(CNR)L₂]Cl (R=p-tolyl; L=PEt₃, PMe₂Ph) in non-polar solvents yielded the Pt formimidoyl complexes *trans*-PtCl(CHNR)L₂. Protonation of *trans*-PtCl(CHNR)(PEt₃)₂ occurred reversibly to produce the cation *trans*-[PtCl(CHNHR)(PEt₃)₂]⁺ while methylation produced *trans*-[PtCl(CHNMeR)(PEt₃)₂]⁺.

Complexes of Platinum and Palladium with Phosphorus Ligands

A. D. RATRAY, *Diss. Abstr. B*, 1976, **36**, (8), 3947-3948

Preparation and interconversion reactions are described for the complexes [M₂X₂(PPh₂O)₂ (PPh₂OH)₂], [MX(PPh₂O)(PPh₂OH)₂], [MX(PPh₂O)(PPh₂OH)(PR₃)], [MX₂(PPh₂P(O)Ph₂)₂], where M=Pd or Pt, X=chloride or bromide; Ph=phenyl, and R=phenyl or ethyl. The complex [PtCl(Phen)(PEt₃)₂]BF₄, containing in the solid state the first known example of a monodentate phenanthroline ligand, was also isolated and is described.

Study of Catalytic Properties of Platinum-Tin Complexes with Dimethyl Sulphoxide, Dimethyl Formamide or Dimethyl Acetamide

N. V. BORUNOVA, P. G. ANTONOV, YU. N. KUKUSHKIN, YA. G. MUKHTAROV, A. N. SHAN'KO and L. KH. FREIDLIN, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1976, (5), 971-975

Studies of a series of new Pt(II)-Sn(II) complexes containing dimethyl acetamide and dimethyl formamide show their considerably higher activity in isomerisation and hydrogenation of C=C containing compounds than that of Pt-SnCl₃ complex. All the studied complexes were found to catalyse the selective hydrogenation of phenylacetylene to styrene and diphenylacetylene to diphenylethane.

Carboxylates of Divalent Rhodium

L. A. NAZAROVA and A. G. MAIOROVA, *Zh. Neorg. Khim.*, 1976, **21**, (4), 1070-1074

New dimeric Rh(II) complex compounds with metal-metal bonds were synthesised. The general formula is Rh₂(Ac)₄A₂, where Ac is HCOO⁻ or CHCOO⁻ and A is an organic complex containing various functional groups, benzene ring and unsaturated atoms.

ELECTROCHEMISTRY

Kinetics of the Hydrogen Electrode Reactions on Platinum in the NaHSO₄+KHSO₄ Eutectic Melt

R. O. LEZNA, W. E. TRIACI and A. J. ARVIA, *J. Electroanal. Chem. Interfacial Electrochem.*, 1976, **71**, (1), 51-71

The kinetics of the H₂ electrode reactions on Pt wire in the NaHSO₄ and KHSO₄ melt were studied at ~185°C. Under potentiodynamic conditions both the anodic and cathodic processes can be interpreted with the H₂ electrode reaction mechanism already known. The mechanism of the cathodic reaction changes at <0.1V because of a sulphide species formed on the electrode, which is produced by a reduction of the melt components.

E.M.F. Measurements of Cells Employing Metal-Metal Oxide Electrodes in Aqueous Chloride and Sulphate Electrolytes at Temperatures between 25–250°C

J. V. DOBSON, P. R. SNODIN and H. R. THIRSK, *Electrochim. Acta*, 1976, **21**, (7), 527–533

E.M.F. measurements were made on Pt-PtO₂, Ir-IrO₃, Rh-Rh₂O₃ and Zr-ZrO₂ electrodes at 25–250°C and pH 1–12 using aqueous chloride and sulphate electrolytes. The results showed an O₂ and sulphate response at 25°C for a Pt-PtO₂ electrode in concentrated H₂SO₄. The effects of temperature, pressure, concentration and time are discussed.

ELECTRODEPOSITION AND SURFACE COATINGS

Precious Metal Plating

H. GROSSMANN and G. SCHAUDT, *Galvanotechnik*, 1976, **67**, (4), 292–297

Studies of Pd, Ru, Rh, and hard Au coatings electrodeposited on electrotechnical connecting components show that Pd deposits perform best in abrasion tests. Ru and Rh deposits were found satisfactory in rotary switches and in plug and socket connectors. Pd deposits applied in sliding and plug contacts show similar wear resistance to hard Au deposits.

The Chemistry of Palladium-Tin Colloid Sensitising Processes

R. L. COHEN and R. L. MEEK, *J. Colloid Interface Sci.*, 1976, **55**, (1), 156–162

Mössbauer spectroscopic studies were made of the chemical composition of layers deposited on graphite substrates by commercial Sn-Pd sensitising system. The results showed that the catalytic centres consist of colloidal particles of Pd-Sn alloy and that the primary purpose of the "accelerator" step in the process is to remove Sn hydroxide deposits.

LABORATORY APPARATUS AND TECHNIQUE

Molecular Beam Apparatus with Supersonic O₂ Beam (700–3000 m/sec) for Reactive Scattering Experiments with Metal Atoms

C. B. COSMOVICI, K. W. MICHEL, R. DIRSCHERL and U. STANGGASSINGER, *Rev. Sci. Instrum.*, 1976, **47**, (6), 667–676

A simple alignable nozzle source for mass spectrometric detection systems consists of a pinhole in the wall of a U-shaped Pt tube which is closed at one end and connected to the gas inlet at the other. When the nozzle, which can withstand corrosive O₂ and can be heated directly, is used in conjunction with a thermal oven, beam collisional energies from 0.1 to 1eV can be obtained.

Mercury Thermometers – Are They Becoming Antiques?

B. W. MANGUM, *N.B.S. Tech. News Bull.*, 1976, **60**, (2), 13–17

Electronic thermometers for medical applications employing either thermistors or Pt resistors have been developed, and the working principles are described. The accuracy is ~0.1°C.

Radiative Heat Transfer from Metal Wires: Hemispherical Total Emittance of Platinum

B. J. JODY and S. C. SAXENA, *J. Phys. E: Sci. Instrum.*, 1976, **9**, (5), 359–362

Data of the radiative heat transfer from Pt at 400–1500K measured on a general hot wire apparatus were analysed to determine the hemispherical total emittance of Pt as a function of temperature. The use of such an instrument for the determination of electrical resistivity of metal wires at high temperature is discussed.

Conductivity Cell for Molten Glasses and Salts

F. G. K. BAUCKE and W. A. FRANK, *Glastech. Ber.*, 1976, **49**, (7), 157–161

An immersion or dip-type cell incorporating two parallel Pt electrodes was developed for conductivity measurements of molten glasses and salts. A cylindrical volume of the melt is enclosed by a ceramic or SiO₂ tube and subjected to the homogeneous and uniform electric field between the electrodes. The cell also allows measurement of local conductivities within technical glass melting units.

Electrical Conductivity Measurements on Silicate Melts Using the Loop Technique

H. S. WAFF, *Rev. Sci. Instrum.*, 1976, **47**, (7), 877–879

The electrical conductivity of silicate melts was measured at up to 1550°C by a technique using loops of 0.635 mm diameter 80%Pt–20%Rh wire. The melt samples are suspended as droplets on the loops and maximum surface exposure results in rapid equilibration of the melt with the controlled atmosphere. This technique gives reproducible results to ±5% and is suitable for electrical conductivity studies on silicate melts containing redox cations.

The Choice of Cathode Material in a Hot Cathode Ionisation Gauge

P. E. GEAR, *Vacuum*, 1976, **26**, (1), 3–10

Studies of cathode materials for use in an u.h.v. gauge showed that cathodes of ThO₂ on Ir or W have reasonable emission efficiencies, low evaporation rates and are relatively unaffected by chemically active gases. The ThO₂ on Ir cathode can be exposed to air when hot without damage, which makes it particularly useful for ionisation gauge applications.

HETEROGENEOUS CATALYSIS

Ammonia Oxidation over Platinum-promoted Oxide Catalysts

N. I. IL'CHENKO, *Kinet. Kataliz*, 1976, **17**, (2), 386-391

Studies of low temperature NH₃ oxidation to N₂ and N₂O over oxide catalysts show that additions of 0.1% Pt to Co₃O₄, MnO₂ and V₂O₅ increase considerably their catalytic activity. The selectivity of the process remains almost unchanged. It is suggested that Pt facilitates the activation of NH₃ molecules and increases the rate of reduction of the oxide catalysts.

Study of Hydrogenation Reactions with Rhodium and Platinum Catalysts Supported on Ion Exchange Resins

S. SABADIE and G. DESCOTES, *Bull. Soc. Chem. Fr.*, 1976, (5-6), 911-913

Studies of the activity of Pt and Rh catalysts supported on ion exchange resins made during hydrogenation of cyclohexene, alkyl alcohol, carvone and phenylacetylene showed better selectivities than the ones obtained with the catalysts supported on charcoal. The influence of the metallic ions on the process is described.

On the Electrolytic Mechanism of Liquid-phase Propene Oxidation over Palladium Catalysts

KH. KINTSA and L. P. MASHKOVA, *Kinet. Kataliz*, 1976, **17**, (2), 362-366

A potentiodynamic method was used to study the oxidation of propene and reduction of O₂ on dispersed Pd and Au-Pd alloys. It is shown that the Pd-Au catalysts have higher catalytic activity in the reaction of propene oxidation than the pure catalyst, with 25 at. % Au-Pd most active.

Synthesis of Cyclododecane by Cyclododecanone Epoxide Isomerisation on Pd and Rh

F. A. CHERNYSHKOVA and D. V. MUSHENKO, *Neftekhimiya*, 1976, **16**, (2), 250-254

The isomerisation of cyclododecane epoxide leading to the formation of cyclododecanone was carried out on supported Pd and Rh catalysts and also on Al₂O₃, SiO₂ and zeolite catalysts. The results show that only Pd and Rh supported on Al₂O₃ and C give high (80-83%) cyclododecanone yields at 245-265°C in H₂ atmosphere.

Transformations of Cyclohexane with Water Vapour on Alumina-Rhodium Catalyst

V. N. MOZHAIKO, G. L. RABINOVICH and G. N. MASLYANSKII, *Neftekhimiya*, 1976, **16**, (1), 45-50

The transformations of cyclohexane with H₂O vapour were studied over a 0.6 wt. % Rh/Al₂O₃ catalyst. It is shown that dehydrogenation and decomposition of cyclohexane take place at 380-460°C. The activation energy of dehydrogenation was found to be 23 kcal/mole. The

selectivity of dehydrogenation increases with a decrease in both temperature and H₂O : cyclohexane ratio. At 420°C and H₂O : cyclohexane ratio of 4 the selectivity reaches 95 mole %.

Methylcyclohexane Transformations with Water Vapour to Aromatic Hydrocarbons on Alumina-Rhodium Catalyst

G. L. RABINOVICH and V. N. MOZHAIKO, *Neftekhimiya*, 1976, **16**, (2), 187-193

Transformations of methylcyclohexane with H₂O vapour over 0.6 wt. % Rh/ γ -Al₂O₃ catalyst at 400-480°C with a molar ratio of H₂O : methylcyclohexane of 4 to 12 were studied. The transformation takes place in three parallel reactions: dehydrogenation leading to toluene formation, dehydrodemethylation leading to benzene formation and decomposition resulting in C oxides formation. The total output of aromatic hydrocarbons is > 80 mol. %.

Alkane and Cycloalkane Reactions on Rhodium, Rhodium-Copper and Related Films

A. PÉTER and J. K. A. CLARKE, *J. Chem. Soc., Faraday Trans. I*, 1976, **72**, (5), 1201-1211

Studies of the catalytic reaction of *n*-hexane-H₂ mixture on Rh-Cu alloy films at ~570K showed the dehydrocyclisation/hydrogenolysis product ratio is one order of magnitude greater than that found on 100% Rh films. 1.5-cyclisation occurs on Rh-Cu films and also on Rh-Au and Rh-Sn films. Ring enlargement of methylcyclopentane and of 1.1-dimethylcyclopentane occurs above ~540K on both Rh and Rh-Cu films.

Mechanism of the Catalytic Effect of Osmium Compounds on the Oxidation of Copper(II) with Periodate

G. I. ROZOVSKII, Z. A. POSHKUTE and A. YU. PROKOPCHIK, *Zh. Neorg. Khim.*, 1976, **21**, (5), 1248-1251

The catalytic effect of OsO₄ on the oxidation of Cu(II) with periodate was studied. It is shown that the catalysis involves the oxidation of Os(VII) to Os(VIII) with periodate, followed by the reduction of the oxidised form of Os by Cu(II). The reaction of Os(VIII) and Cu(II) was found to be reversible.

HOMOGENEOUS CATALYSIS

Catalytic Asymmetric Hydrosilylation of Ketones. I. Chiral Phosphine-Platinum(II) Complex-catalysed Hydrosilylation

T. HAYASHI, K. YAMAMOTO and M. KUMADA, *J. Organometal. Chem.*, 1976, **112**, (3), 253-262

Studies of the hydrosilylation of alkyl phenyl ketones and dialkyl ketones with HSiMeCl₂ in the presence of the [(PhMe₂P)PtCl₂]₂ catalyst showed good yields of corresponding silyl ethers of

1-phenylalkanols and silyl enol ethers respectively. Asymmetric hydrosilylation of a series of alkyl phenyl ketones catalysed by chiral phosphine-Pt(II) complexes was studied.

Palladium-catalysed Dibenzofuran Synthesis by Dehydrogenative Ring Closure

A. SHIOTANI and H. ITATANI, *J. Chem. Soc., Perkin Trans. I*, 1976, (11), 1236-1241

Studies of the dehydrogenation of diphenyl ethers in the presence of a Pd acetate catalyst showed that under O₂ pressure the coupling proceeds with a catalytic quantity of Pd acetate to give dibenzofuran in higher yields relative to dimers. The regeneration of the Pd acetate is described.

CHEMICAL TECHNOLOGY

The Effect of Nickel and Palladium Additions on the Activated Sintering of Tungsten

R. M. GERMAN and V. HAM, *Internat. J. Powder Metall. Powder Technol.*, 1976, 12, (2), 115-125

Studies of sintering processes on two different W powders show that Pd is a better sintering activator than Ni at 1100-1400°C. Both Pd and Ni give best shrinkage enhancement when present at the quantity of four atomic monolayers.

NEW PATENTS

METALS AND ALLOYS

Alloys Containing Platinum Group Metals

JOHNSON MATTHEY & CO. LTD.

French Appl. 2,277,903

Apart from impurities, the alloy contains at least 40% Ni or Co, a trace to 30% Cr and a trace to 15% of one or more of Pt, Pd, Rh, Ir, Os and Ru. The alloy is useful for manufacturing reaction motor parts and gas turbines.

ELECTROCHEMISTRY

Seawater Electrolysis Cathode

ELECTRONOR CORP.

U.S. Patent 3,947,333

A cathode for a cell has an electrically conductive electrode base with an outer coating, on at least a portion of its surface, of an alloy of Pd and 10-50% of either Ag or Pb.

Iridium Thin Ribbon Electrodes for Electrochemical Cells

E. I. DU PONT DE NEMOURS & CO.

U.S. Patent 3,954,590

An electrolytic moisture detection cell consists of a substrate and spaced thin ribbon metal electrodes having a thickness of 0.1-1.0 μm attached

ELECTRICAL AND ELECTRONIC ENGINEERING

Electroetching of Platinum in the Titanium-Platinum-Gold Metallisation on Silicon Integrated Circuits

R. P. FRANKENTHAL and D. H. EATON, *J. Electrochem. Soc.*, 1976, 123, (5), 703-706

A rapid electrolytic method of etching patterns in Pt on semiconductor slices is described, a periodically varying potential being applied to the Si wafer immersed in HCl solution at room temperature. The dissolved Pt can be recovered and the process is also applicable to the etching of metallisations on other high-resistance substrates.

Hydrogen-sensitive Palladium Gate MOS Capacitors

M. C. STEELE, J. W. HILE and B. A. MACIVER, *J. Appl. Phys.*, 1976, 47, (6), 2537-2538

The C-V characteristics of Pd gate MOS capacitors using thin Pd films (100Å) on thin oxide layers (100-1000Å) change considerably when exposed to an air ambient containing up to 4% H₂. The changes are attributed to the lowering of the Pd work function brought on by the formation of Pd hydride.

to and supported by the substrate. The electrodes consist of an anode and a cathode, the cathode being formed by Ir or an alloy containing at least 10% Ir and the remainder Pt. A hygroscopic film is deposited on the substrate and fills at least a portion of the space between the anode and the cathode.

ELECTRODEPOSITION AND SURFACE COATINGS

Thin Layers of High Melting Point Materials

SIEMENS A.G.

British Patent 1,442,109

A thin layer of Os, W, Mo or Re is produced on a substrate by evaporating the (IV) oxide of the metal under a high vacuum while heating the substrate.

Chemical Plating Catalyst

A.M.P. INC.

U.S. Patent 3,937,857

A substrate is catalysed for chemical plating by applying and then thermally decomposing a thin film of a complex L_mPdX_n or the corresponding Pt complex. L is a ligand or unsaturated organic group, X is halide, alkyl or a bidentate ligand, m is 1-4 and n is 0-3. A typical complex is Pd bis-triphenylphosphine dichloride.