

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Migration of Platinum Adatom Clusters on Tungsten (110) Surfaces

D. W. BASSETT, *J. Phys. C: Solid State Phys.*, 1976, 9, (13), 2491-2503

The migration of Pt atoms and clusters of two to four atoms adsorbed on W(110) was studied using field-ion microscopy. The results show that the mobility decreases with increasing cluster size. The activation energies for motion were found to be 65 ± 6 kJ/mole for Pt and Pt₂, 77 ± 15 kJ/mole for Pt₃ and 84 ± 15 kJ/mole for Pt₄.

The Adsorption of Nitric Oxide on Pt(111) and Pt(110)

C. M. COMRIE, W. H. WEINBERG and R. M. LAMBERT, *Surface Sci.*, 1976, 57, (2), 619-631

LEED, Auger spectroscopy and thermal desorption were used to study the thermal and electron impact behaviour of NO adsorbed on Pt(111) and Pt(110). The results show that NO adsorbs non-dissociatively and has similar low coverage adsorption enthalpies on both surfaces at 300K. The (111) surface was significantly more active in inducing the thermal dissociation of NO. Electron impact effects were also much more important on this surface. The results are compared to those previously obtained for NO adsorption on Ni(111) and Pd(111).

Electrical Properties of Platinum in Silicon as Determined by Deep-level Transient Spectroscopy

A. O. EYWARAYE and E. SUN, *J. Appl. Phys.*, 1976, 47, (7), 3172-3176

Electrical properties of Pt diffused in to p⁺ nn⁺ and n⁺ pp⁺ Si diodes at 860-910°C were studied using deep-level transient spectroscopy. Thermal emission rates of trapped electrons, trapped holes, activation energies, defect concentrations and capture cross sections for majority carriers in n- and p-type Si:Pt junctions are reported.

Magnetic and Nonmagnetic Impurities in Some A-15 Structure Systems. I. Superconducting Properties. II. Magnetic Properties

G. H. BONGI, R. FLÜKIGER, A. TREYVAUD and Ø. FISCHER, *J. Low Temp. Phys.*, 1976, 23, (5/6), 543-569; 571-597

Measurements of the critical temperature T_c and the critical field H_{c2} of the A-15 structure systems Nb_yPt_{100-y-x}M_x, where M=Fe and Ru, (y=73 to 78), were carried out by a standard

induction bridge. It is shown that there is a non-magnetic contribution of Fe and Ru impurities to the T_c decrease and that the magnetic moment of the Fe atoms depends on the sites where the Fe atoms are situated. Measurements of the susceptibility combined with those of the critical temperature T_c show that there is a saturation of the effective number of magnetic impurity atoms. The magnetic moment of the Fe atoms depends on the value of y.

The Limiting Stage of Hydrogen Permeability through Palladium Alloys Membranes

YU. K. BAICHTOK, YU. A. SOKOLINSKII and M. B. AIZENBUD, *Zh. Fiz.Khim.*, 1976, 50, (6), 1543-1546

Kinetic studies of H₂ permeability through Pd-23% Ag, Pd-20% Ag and Pd-10% Ag-5.5% Ni membranes show that depending on the conditions, the rate limiting steps for the process are either the dissociation of H₂ on the membrane surface or diffusion. In the first case the diffusion is proportional to the H₂ pressure p and in the second case to p^{1/2}. It is shown that the diffusion rate increases by a factor of 2 for 0.1 mm thick Pd-10%Ag-5.5% Ni membrane at 500°C and H₂ pressure of 5 atm, as a result of increasing the degree of surface activation.

Anomalous Temperature Dependence of Electrical Resistance of Palladium-Iron Alloys

E. V. PAL'GUEV, A. A. KURANOV, P. N. SYUTKIN and F. A. SIBORENKO, *Fiz. Metal. Metalloved.*, 1976, 42, (1), 57-61

The temperature dependence of electrical resistance of ordered 49-78 at.% Pd-Fe alloys at 300-1300K was studied. It is shown that on ordering the specific resistance ρ increases with temperature for all alloy compositions with an exception of stoichiometric PdFe. This anomalous increase in ρ is independent of the crystal and domain structure of the ordered phase.

The Reaction of Tellurium Tetrachloride with Iron, Cobalt, Nickel, Palladium and Manganese Dichlorides

A. V. KONOV and V. V. SAFONOV, *Zh. Neorg.Khim.*, 1976, 21, (7), 1979-1981

Reactions in systems including PdCl₂-TeCl₄ and MnCl₂-TeCl₄ were studied using differential thermal analyses. In the system PdCl₂-TeCl₄ a eutectic point occurs at 90 mol.% TeCl₄ and 215°C. The decrease in crystallisation temperature of the eutectic observed at 0-40 mol.% TeCl₄ is due to the formation of a solid solution based on PdCl₂.

Short-range Structures of Amorphous and Liquid Iron and Pd_{0.8}-Si_{0.2} Alloy

K. SUZUKI, T. FUKUNAGA, M. MISAWA and T. MASUMOTO, *Sci. Reports Res. Inst. Tôhoku Univ. A*, 1976, **26**, (1), 1-11

X-ray diffraction studies of Pd_{0.8}-Si_{0.2} alloy in amorphous and liquid states show an entirely different Si-Si correlation in both these states. The atomic configuration for the nearest neighbour Pd-Pd and Pd-Si in amorphous Pd_{0.8}-Si_{0.2} was found close to that in Pd₃Si orthorhombic crystal. The existence of partial short-range order in the amorphous Pd_{0.8}-Si_{0.2} is suggested.

Atomic Diffusion of Lithium in an Amorphous Metallic Pd-Si Alloy

C. BIRAC and D. LESUEUR, *Phys. Status Solidi A, Appl. Res.*, 1976, **36**, (1), 247-251

The diffusion coefficient of Li in an amorphous metallic Pd₈₀Si₂₀ alloy obtained by rapid quenching from the melt was measured at 240-290°C and found to be 6×10^{-14} to 2×10^{-16} cm²/sec. Li diffusion is at least 10⁸ times faster in the amorphous alloy than in the crystalline alloy.

A Study of Corrosion Resistance of Titanium and Vanadium Based Alloys with Rhenium and Ruthenium Additions

A. YU. KHANNA, V. K. YURTAEVA, M. V. RAEVSKAYA and E. M. SOKOLOVSKAYA, *Vest. Moskov. Univ., Ser. II, Khim.*, 1976, **17**, (2), 204-207

Polarisation curves were used to study the corrosion resistance of Ti and V based alloys with 0-10% Re and/or Rh additions in 20-30% HCl at 25°C. It was found that the additions increase the corrosion resistance of Ti and V.

Electrical Resistivity Studies of the Magnetic Character of Rh-Co Alloys

A. TARI, *J. Phys. F: Metal Phys.*, 1976, **6**, (7), 1313-1323

Studies of the low temperature resistivity of Rh-Co alloys containing 11-42 at.% Co showed the stabilisation occurring at ~20 at.% Co which was due to local environment effects. The alloys containing 28-36 at.% Co showed the transition into a spin glass phase. In alloys >36 at.% Co itinerant type ferromagnetism appeared.

The Vanadium-Ruthenium Constitution Diagram

R. M. WATERSTRAT and R. C. MANUSZEWSKI, *J. Less-Common Metals*, 1976, **48**, (1), 151-158

Studies have been made of the Ru-V system over the entire range of composition and the proposed constitution diagram is presented. The system appears to be a simple eutectic with the reaction occurring at $1790 \pm 10^\circ\text{C}$ and 40 at.% Ru while the ϵ -Ru solid solution extends to 31 at.% V at high temperatures but less than 20 at.% V below about 1100°C ; the α -V solid solution extends to about 55 at.% Ru at the eutectic temperature.

LEED, AES and Thermal Desorption Studies of Chemisorbed Hydrogen and Hydrocarbons (C₂H₂, C₂H₄, C₆H₆, C₆H₁₂) on the (111) and Stepped [6(111) × (100)] Iridium Crystal Surfaces; Comparison with Platinum

B. E. NIEUWENHUYNS, D. I. HAGEN, G. ROVIDA and G. A. SOMORJAI, *Surface Sci.*, 1976, **59**, (1), 155-176

Studies of the adsorption of H₂, ethylene, acetylene, cyclohexane and benzene on both the (111) and stepped [6(111) × (100)] crystal surfaces of Ir show that decomposition of the H₂ occurs more easily on the stepped Ir surface than on the (111) surface. H₂ is desorbed at a higher temperature from an Ir surface with high density of surface imperfections than from a perfect Ir(111) surface. Comparison with results obtained previously on similar crystal surfaces of Pt shows that C-H bond breaking is easier on Ir than on Pt.

CHEMICAL COMPOUNDS

Thermal Transformation of Dimeric Platinum(II) Complexes

YU. N. KUKUSHKIN, G. S. KRYLOVA, G. N. KVASOVA and V. P. KOTEL'NIKOV, *Zh. Neorg. Khim.*, 1976, **21**, (7), 1951-1952

The thermal transformations of [PtLen][PtX₄] and [PtL₂][PtX₄] complexes where L=dithioesters or aminothioesters and X=Cl or Br were studied and the values of enthalpies and activation energies were derived. It is shown that substitution of one dithioester ligand by ethyleneamine causes an increase in both the transformation temperature and the activation energy.

A cis-Dihydride of Platinum(II)

C. J. MOULTON and B. L. SHAW, *J. Chem. Soc., Chem. Commun.*, 1976, (10), 365-366

The preparation and characterisation of a cis-dihydride of Pt(II) is reported for the first time.

Linear Metal Chain Complexes. Structural Characterisation of Bis(pyridine-2-methylcarboxaldoximinato)platinum(II)

D. W. PHELPS, W. F. LITTLE and D. J. HODGSON, *Inorg. Chem.*, 1976, **15**, (9), 2263-2266

Crystal structure studies of Pt(C₇H₇N₂O)₂ show it to be orthorhombic, space group *Pbcn* with four formula units in a cell of dimensions $a=12.410$, $b=15.763$ and $c=6.727\text{Å}$. The structure consists of linear chains of planar Pt(C₇H₇N₂O)₂ units which are parallel to the *c* axis and have Pt-Pt separation of 3.363Å. The complex shows enhanced electrical conductivity which is of the same magnitude as that of Magnus green salt.

Crystal Structure of Sodium Platinates (IV)

J. HAUCK, *Z. Naturf. B*, 1976, **31**, (9), 1177-1182

Thermal reactions of Pt powder with Na oxide or peroxide yielded cubic γ -Na₃PtO₃ ($a=4.487\text{Å}$), Na₄PtO₄ ($a=4.52\text{Å}$) and tetragonal Na₃PtO₆.

($a=7.965$, $c=4.053\text{\AA}$) compounds. Their crystal structures could be related to the NaCl structure with partial ordered superstructure in Na_3PtO_6 or without long range ordering in $\gamma\text{-Na}_2\text{PtO}_3$ and Na_4PtO_4 .

The Crystal Structure of Bis(histamino)-palladium Dichloride, $(\text{N}_3\text{C}_5\text{H}_9)_2\text{PdCl}_2$

F. DAHAN, *Acta Cryst. B*, 1976, **32**, (8), 2472-2475
Crystal structure studies of $(\text{N}_3\text{C}_5\text{H}_9)_2\text{PdCl}_2$ showed it to be monoclinic, space group $P2_1/c$ with $a=9.124$, $b=9.687$, $c=9.191\text{\AA}$, $\beta=109.26^\circ$ and $Z=2$. The Pd atom is in a square-planar arrangement. The Pd-N lengths are 2.057 and 2.029\AA for Pd-N(3) and Pd-N(1) respectively.

ELECTROCHEMISTRY

Oxidation of Primary Amines Bound to Bis(2,2'-bipyridine)ruthenium(II)

F. R. KEENE, D. J. SALMON and T. J. MEYER, *J. Am. Chem. Soc.*, 1976, **98**, (7), 1884-1889

It is shown that chemical and electrochemical oxidations of the ions $[\text{Ru}(\text{bpy})_2(\text{NH}_2\text{CH}_2\text{R})_2]^{2+}$ where $\text{NH}_2\text{CH}_2\text{R}$ =allylamine, benzylamine or *n*-butylamine, occur by dehydrogenation at the amine ligands giving the corresponding bis(nitrile) complexes, $[\text{Ru}(\text{bpy})_2(\text{N}\equiv\text{CR})_2]^{2+}$.

Electrochemical Behaviour of Pd-In Alloys in Some Electroreduction Processes

A. M. MERETSKII, I. V. KUDRYASHOV, E. M. SAVITSKII, V. P. POLYAKOVA and N. B. GORINA, *Izv. Akad. Nauk S.S.S.R., Metall.*, 1976, (5), 193-196

Studies of the cathodic H_2 evolution and electroreduction of nitromethane, CH_3NO_2 , on 40-53 at.% In-Pd electrodes show that the catalytic activity of the alloy is by one order of magnitude higher than that of pure Pd. The highest catalytic activity was found for the alloy containing 50 at.% In.

ELECTRODEPOSITION AND SURFACE COATINGS

Differential Capacitance of Palladium and Electrodeposited Palladium on Pyrolytic Graphite Electrodes in Aqueous Solutions

I. MORCOS, *J. Electroanal. Chem. Interfacial Electrochem.*, 1976, **72**, (3), 389-395

The differential capacitance of both massive Pd and electrodeposited Pd/pyrolytic graphite electrodes were measured in alkaline and acid media using spectroscopy and linear sweep voltammetry. All the capacitance curves for the electrodeposited Pd/graphite were characteristic of the current density at which the Pd was deposited. With a low current density of 4.5 mA/cm², the capacitance curve was similar to that observed on massive Pd.

The Formation and Reduction of Anodic Films on Electrodeposited Ruthenium

L. D. BURKE and J. K. MULCAHY, *J. Electroanal. Chem. Interfacial Electrochem.*, 1976, **73**, (2), 207-218

The formation and reduction of anodic films were studied on Ru plated electrodes prepared by the electrodeposition of Ru on to Au plated Pt substrates at 70°C. The bell-shaped cathodic current-time curves observed with films produced at $\sim 1.2\text{V}$ showed the nucleation of reduction centres. The influence of potential, time, and both the concentration and the nature of the electrolyte on anodic film formation were studied.

LABORATORY APPARATUS AND TECHNIQUE

Continuous Oxygen Measurement in Tank Combustion Atmospheres

J. T. BROWN, J. W. HOSKINS and A. M. CHIRINO, *Glass Ind.*, 1976, **57**, (7), 12-15

A platinised, yttria-stabilised zirconia sensor which allows monitoring of glass furnace O_2 concentration without removing a sample of the gas from the furnace has been developed. The sensor was tested successfully in furnaces producing borosilicate glasses, glass-ceramics and soda-lime glasses at 750-1550°C. The sensor has a life > 6 months and the accuracy of measurement is within $\frac{1}{2}\%$ O_2 compared with an off-site analyser.

Detection of H_2S with Pd-gate MOS Field-effect Transistors

M. S. SHIVARAMAN, *J. Appl. Phys.*, 1976, **47**, (8), 3592-3593

Studies of the sensitivity of Pd-gate MOS field-effect transistors to H_2S in air showed that the transistor can detect even small amounts of H_2S in air. The threshold voltage change of the transistor at 150°C caused by 50 p.p.m. H_2S in air was $\sim 30\text{mV}$.

HETEROGENEOUS CATALYSIS

The Dehydrogenation and Hydrogenolysis of Cyclohexane and Cyclohexene on Stepped (High Miller Index) Platinum Surfaces

D. W. BLAKELY and G. A. SOMORJAI, *J. Catalysis*, 1976, **42**, (2), 181-196

Studies of cyclohexane and cyclohexene dehydrogenation and hydrogenolysis on stepped Pt single crystal surfaces at 10^{-6} torr and 300-723K were carried out. It was found that atomic steps and kinks are active sites for C-H and H-H bond breaking processes, and for C-C bond scission. During the catalytic reactions the Pt surface became partially or completely covered with a layer of carbonaceous deposit which was ordered

or disordered and whose properties influenced both the resistance to poisoning and the product distribution of the catalytic reactions.

The Effect of Different Atmospheres on the Sintering of Pt/Al₂O₃ Reforming Catalysts

S. A. HASSAN, F. H. KHALIL and F. G. EL-GAMAL, *J. Catalysis*, 1976, **44**, (1), 5-14

Studies have been made of the effect of H₂, O₂ and N₂ atmospheres, gases widely used in many petrochemical processes, on the sintering of Pt/Al₂O₃ reforming catalysts in the range 300-800°C. Below 400°C the results were similar to those for unsupported Pt. Treatment in N₂ and H₂ above this temperature can lead to activation, but in O₂ the activity decreased.

The Effect of Solvents on the Course of Hydrogenation of 1-Phenyl-2-propene and 4-Nitrotoluene on a Platinum Catalyst

L. ČERVENÝ and V. RŮŽIČKA, *Coll. Czech. Chem. Commun.*, 1976, **41**, (7), 1894-1897

Hydrogenation of 1-phenyl-2-propene and 4-nitrotoluene over 5% Pt/SiO₂ gel catalyst was carried out in a series of solvents. Both the individual substrates and their equimolar mixture were hydrogenated. The effects of solvents on the rate and selectivity of the hydrogenation of the equimolar mixture are discussed.

The Sintering of Supported Metal Catalysts. I. Redispersions of Supported Platinum in Oxygen

R. M. J. FIEDOROW and S. E. WANKE, *J. Catalysis*, 1976, **43**, (1-3), 34-42

Studies of the effect of treatment in O₂ of 0.5-4.0 wt.% Pt/Al₂O₃ catalysts on the Pt dispersion show that at ≤600°C a significant increase in dispersion occurs. At 500 and 550°C the increases in dispersion were found to be independent of the length of treatment. At ≥600°C decreases in dispersion occurred which were a strong function of treatment time and temperature. The molecular migration model is proposed as the mechanism of sintering for Pt/Al₂O₃ in O₂.

Influence of Nickel-Aluminium Spinel Support on the Activity and Thermostability of Platinum-Rhenium and Platinum-Iridium Catalysts in Cyclohexane Dehydrogenation

N. S. KOZLOV, E. A. SKRIGAN, L. YA. MOSTOVAYA, L. P. DMITRIEVA and M. V. ZARETSKII, *Neftekhimiya*, 1976, **16**, (4), 528-532

Studies of cyclohexane dehydrogenation over Pt, 0.5 wt.% Pt-1.0 wt.% Re and also 0.5 wt.% Pt-0.05 wt.% Ir catalysts supported on NiAl₂O₄ were carried out at atmospheric pressure and 300-350°C. The activity of all the catalysts was found lower and their thermostability higher than those of the same catalysts supported on γ-Al₂O₃ or MgAl₂O₄. This is thought to be due to compound formation between Pt, Ni and Re or Ir.

Direct Evidence for Bimetallic Clusters

R. L. GARTEN, *J. Catalysis*, 1976, **43**, (1-3), 18-33

Mössbauer spectroscopy was used to study the formation of bimetallic clusters in PdFe/η-Al₂O₃ catalysts. The chemical states of Fe on Al₂O₃ in the presence and absence of Pd for various treatments were determined. The Mössbauer parameters, dispersion measurements and the chemical behaviour of Fe in PdFe catalysts confirm the existence of Sinfelt's bimetallic clusters.

1,3 Butadiene Oligomerisation Catalysed by Polymer-attached Palladium Complexes. Comparison with Homogeneous Catalysis

C. U. PITTMAN, S. K. WUU and S. E. JACOBSON, *J. Catalysis*, 1976, **44**, (1), 87-100

Polymer-attached Pd catalysts including PdCl₂, Pd(PPh₃)₄ and Pd(OAc)₂ were synthesised. These complexes were attached to swellable styrene-divinylbenzene resin beads by polymeric triphenylphosphine moieties. The catalytic behaviour of the catalysts was studied in linear dimerisation-acetoxylation of 1, 3-butadiene. It was found that the product distribution was the same as those homogeneously catalysed by PPh₃ plus Pd(OAc)₂ at equal P: Pd ratios. In the presence of triethylamine, metallic Pd was precipitated in the resin.

Polymer-attached Palladium-π-complexes

F. HOJABRI, *J. Appl. Chem. Biotechnol.*, 1976, **26**, (7), 382-384

A new type of Pd homogeneous-heterogeneous catalyst was prepared by attaching Pd(C₆H₅CN)₂-Cl-π-complexes to polymer. The attachment of Pd to the support was performed by two methods: fixation through a phosphine ligand and formation of a π-complex between Pd and polymer support.

The Reduction of Acetonitrile on Rhodium

A. A. SUTYAGINA, T. V. KUL'CHITSKAYA, T. L. BALABONTSEVA and G. D. VOVCHEKNO, *Vest. Moskov. Univ., Ser. II, Khim.*, 1976, **17**, (3), 332-335

Studies of acetonitrile electroreduction and hydrogenation on Rh catalysts with various microstructures showed that the type of microstructure affects the hydrogenation process only.

Activity of Iridium-Ruthenium and Iridium-Rhodium Adsorption Catalysts during the Decomposition of Hydrogen Peroxide

I. A. ZUBOVICH, V. A. MIKHAILOV and N. N. MIGULINA, *Zh. Fiz. Khim.*, 1976, **50**, (6), 1492-1494

The catalytic activity and magnetic susceptibility of Ir-Ru and Ir-Rh catalysts supported on C and SiO₂ were studied during the decomposition of H₂O₂ at 25, 35 and 55°C. The results show that both the observed and additive activities increase with the Ru and Rh contents. The dependence of magnetic susceptibility on composition is discussed in terms of the electronic structure of the catalyst components.

Properties and Influence of Noble-Metal Catalyst on Heterogeneously Catalysed Hydrogenation

G. HORN, C. D. FROHNING and B. CORNILS, *Chem. Z.*, 1976, **100**, (7/8), 299-308

A comprehensive review is given of the properties of Ru, Rh, Pd, Os, Ir and Pt catalysts, supported and unsupported, including their selectivity, the duration of the reactions and the amount of hydrogen. (149 refs.)

Cyclohexane Conversion on Ruthenium Catalysts of Widely Varying Dispersion

Y. L. LAM and J. H. SINNFELT, *J. Catalysis*, 1976, **42**, (2), 319-322

The effect of Ru dispersion on the selectivity of conversion of cyclohexane was studied using an unsupported Ru catalyst and 0.1-5.0 wt.% Ru/SiO₂ catalysts, with various degrees of dispersion. The selectivity increased by more than one order of magnitude when Ru dispersion was increased from 0.006 to unity. This is explained in terms of differences in the nature of the chemisorbed intermediates involved in the hydrogenolysis and dehydrogenation reactions.

HOMOGENEOUS CATALYSIS

Catalytic Asymmetric Hydrosilylation of Olefins. I. Chiral Phosphine-Platinum(II) Complexes as Hydrosilylation Catalysts

K. YAMAMOTO, T. HAYASHI, M. ZEMBAYASHI and M. KUMADA, *J. Organometal. Chem.*, 1976, **118**, (2), 161-181

Catalytic asymmetric hydrosilylation was performed for the first time in the reaction of methylchlorosilane with 1,1-disubstituted prochiral olefins, over [L₂PtCl₂]₂ catalyst (L = (R)-benzylmethylphenylphosphine and (R)-methylphenyl-*n*-propylphosphine), and partly optically active products of RMeCHCH₂SiMeCl₂ where R = Ph, *i*-Pr and Et, were obtained. With trichlorosilane, the asymmetric addition reaction was always accompanied by isomerisation or dimerisation of the olefins.

The Composition of Reduced Palladium Oxide and Its Behaviour as a Catalyst for Liquid Phase Hydrogenation

I. T. CAGA, E. SHUTT and J. M. WINTERBOTTOM, *J. Catalysis*, 1976, **44**, (2), 271-280

Studies of liquid phase hydrogenation of 1-octyne and phenylacetylene over reduced PdO catalyst in C₁- to n-C₄-alcohols and n-C₆- to n-C₈-alkanes as solvents were carried out at 1 atm and at 30°C. The activities of PdO reduced in situ were higher in alcoholic solvents than in the n-alkanes and nonlinear rate-weight relationships were observed. This was thought to be due to an incomplete reduction of the PdO. For prerduced catalysts, linear rate-weight relationships were obtained and better activity in n-hexane than in the alcohols was observed.

Selectivity of a Homogeneous Rhodium-Tin Catalyst in Olefin Transformations

L. KH. FREIDLIN, N. V. BORUNOVA, I. U. NUMANOV, N. YA. TRINK, V. M. IGNATOV, O. L. DROZDOVA and V. A. PETUKHOV, *Neftekhimiya*, 1976, **16**, (4), 508-512

The selectivity of a homogeneous Rh₂Cl₂(SnCl₃)₄ catalyst containing 1.10⁻⁴g atom Rh/(Sn:Rh=3) was studied in isomerisation and hydrogenation of allylbenzene, pentenes and allylacetone. The catalyst is highly active for the transfer of C=C bonds and for *cis-trans* transformations but is practically inactive for hydrogenation.

An Immobilised Rhodium(I) Homogeneous Catalyst

T. H. KIM, *Diss. Abstr. B*, 1976, **37**, (1), 356

A polymer-bound Rh complex catalyst was prepared by attaching a homogeneous hydrogenation catalyst, tris(triphenylphosphine)chlororhodium(I) to a stable aromatic polyamide to produce a catalyst suitable for heterogeneous applications. The polymer-bound catalyst showed the same activity and selectivity as the homogeneous Rh complex catalyst. The possibility of creating many new industrially useful catalysts is discussed.

CATHODIC PROTECTION

Influence of Alloying Elements on the Passivation and the Corrosion Resistance of Iron Chromium Base Alloys

N. D. TOMASCHOW, G. P. TSCHERNOVA, L. A. TSCHIGIRINSKAJA and M. F. GERMAN, *Werkstoffe Korrosion*, 1976, **27**, (9), 636-640

The influence of cathodic alloying with 0.1-0.5% Pd on the passivation and the corrosion resistance of 25-100% Cr-Fe alloys and 25% Cr steels (containing Mn, Ni, Mo and N) was studied in hot concentrated H₂SO₄ and diluted HCl solutions. It is shown that the Pd addition considerably increases the auto-passivation tendency and the corrosion resistance of the alloys.

CHEMICAL TECHNOLOGY

Platinum-Tin Catalysts for Methanol Fuel Cells Prepared by a Novel Immersion Technique, by Electrodeposition and by Alloying

M. M. P. JANSSEN and J. MOOLHUYSEN, *Electrochim. Acta*, 1976, **21**, (11), 861-868

A novel immersion technique developed for the preparation of Pt-Sn electrocatalysts consists of covering a properly pretreated Pt surface with a fraction of a monolayer of Sn without the use of electrical current. Best results were achieved by immersing a H₂-covered Pt electrode into an aqueous Sn solution. The catalysts were compared with commercial Pt-Sn electrodeposits and true Pt-Sn alloys.

ELECTRICAL AND ELECTRONIC ENGINEERING

Control of Palladium Adherence to Silicon Dioxide for Photolithographic Etching

M. S. SHIVARAMAN and C. M. SVENSSON, *J. Electrochem. Soc.*, 1976, **123**, (8), 1258

A method for increasing the adherence of thin Pd film (100 nm) evaporated on to SiO₂ wafer was developed. It consists of annealing the composite in air at 200°C for 30 min, applying a photoresist, spinning, drying, exposure, developing and baking followed by etching with 1:10:10 HCl:HNO₃:CH₃COOH and resist removal in acetone. The air annealing at 200°C is assumed to extract H₂ from the Pd-SiO₂ surface thus increasing the adhesion of the film.

TEMPERATURE MEASUREMENT

The Melting Temperature of Platinum Measured from Continually Melting and Freezing Ribbons

J. BEZEMER and R. T. JONGERIUS, *Physica B+C*, **83**, (3), 338-346

The melting temperature of Pt was measured by using pure Pt ribbons, 2 mm wide and 0.02 mm thick, heated by a modulated direct electric current to the melting point. The melting of a small centre dot of the ribbon during a fraction of the period causes a rise in emissivity of the centre.

NEW PATENTS

METALS AND ALLOYS

Ruthenium Powder Metal Alloy

GENERAL MOTORS CORP. *U.S. Patent* 3,957,451
A sintered powder metal alloy contains about 75-85% Ru dispersed in a matrix of 15-25% of a pre-alloyed composition consisting of 65-80% Ni, 5-10% Cr, 5-15% W, 4-6% Si and 2-6% Fe. The surface of the Ru powder is soluble in the pre-alloyed composition for ductility and has good oxidation and spark erosion resistance at temperatures as high as ~2000°F. The alloys are used for electrical contacts and sparking electrodes.

Modified Iridium-Tungsten Alloy

U.S. ENERGY RESEARCH & DEVELOPMENT ADMINISTRATION *U.S. Patent* 3,970,450
An Ir base alloy composition having enhanced impact resistance consists of 20-50 p.p.m. Al,

The results showed that the radiance temperature at which the melting starts can be measured with a sensitivity of 0.02K. Pt ribbons with a temperature stabilisation can be therefore used for temperature calibration.

Problems in the Measurement of Temperature with Pt-Rh Thermocouples

L. FROSCHAUER and H. SCHMIDT, *Keram. Z.*, 1976, **28**, (7), 346-348

Temperature measurements made with Pt-Rh thermocouples were found to differ depending on the kind of ceramic sheathing used. The changes of e.m.f. observed at above 1300°C in both oxidising and reducing atmospheres were attributed to Fe or Si impurities in the protective ceramic. The use of Al sheaths with 99.7% Al₂O₃ was recommended.

MEDICAL USES

Complexation of Tetra-μ-carboxylato-dirhodium(II) with Imidazole

K. DAS and J. L. BEAR, *Inorg. Chem.*, 1976, **15**, (9), 2093-2095

The formation constants, the enthalpies and entropies of reactions for the formation of 1:1 and 1:2 adducts of Rh₂(O₂CR)₄ where R = CH₃OCH₂, CH₃ or CH₃CH₂ with imidazole were determined. The order of stability was found to be propionate > acetate > methoxyacetate. The Rh(II) carboxylates were found to have high anti-tumour activity.

20-100 p.p.m. Fe, 5-20 p.p.m. Ni, 50-100 p.p.m. Rh, 15-50 p.p.m. Th and Ir as the balance.

Palladium-Silver Alloy for Use in Nuclear Reactors

COMMISSARIAT A L'ENERGIE ATOMIQUE

French Appl. 2,285,172

For the introduction of gaseous H₂ into H₂O, such as for the hydrogenation of pressurised H₂O in a nuclear reactor, a helicoidal tube of a 77% Pd-23% Ag alloy is employed.

CHEMICAL COMPOUNDS

Intermetallic Ferromagnetic Compounds

INTERNATIONAL BUSINESS MACHINES CORP.

British Patent 1,450,889

The compounds have the general formula R₂TX where R is Rh or Ru, T is Fe, Co, Ni, V, Cr or Cu and X is Al, Ga, In, Tl, Ge, Sn or Sb.