

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Electrical Resistance of Platinum Wires during Annealing and Quenching in Air and Helium

J. POLAK and L. KUNZ, *Czech. J. Phys.*, 1971, **21**, (3), 269-274

The electrical resistance of Pt wires annealed and quenched in air and He was measured. Irreversible changes in the resistance were observed in specimens treated in air, but not in those treated in He. The changes are partly due to dimensional changes on oxidation, for which the activation energy is 1.79 ± 0.04 eV.

Dispersion Hardened Platinum and Gold Alloys for Electrical Applications

M. L. GIMPL and N. FUSCHILLO, *J. Metals*, 1971, **23**, (6), 39-44

Dispersion hardened alloys of Pt and Au containing ThO_2 and Al_2O_3 were made by precipitating the elements from solution on to a suspension of oxide particles. The alloys showed good homogeneity but contained large amounts of adsorbed gases which were removed by heating in vacuo. Optimum mechanical properties were obtained with 1-2 vol.% dispersoid. Dispersion strengthening slightly increases resistivity.

Reaction of Sulphur and Sulphur-containing Substances with Platinum, Rhodium and Platinum-Rhodium Alloys

G. ZWINGMANN and E.-M. WENZEL, *Metall*, 1971, **25**, (10), 1121-1123

Pt-Rh alloys and pure Rh react at 800-1200°C rapidly with H_2S , but only slowly with SO_2 with formation of sulphides. No reaction occurs with K_2SO_4 .

Processes of Ordering and the High Coercivity State of CoPt Alloy

G. V. IVANOVA, L. M. MAGAT, L. V. SOLINA and YA. S. SHUR, *Fiz. Metal. Metalloved.*, 1971, **32**, (3), 543-548

The greatest coercivity of CoPt is related to the state in which mainly the ordered phase is present. Annealing in two stages at 700 and 600°C gives better magnetic properties than single-stage annealing because a homogeneous structure is formed during the first stage with further ordering during the second stage.

Interaction of Hydrogen with Palladium

A. W. ALDAG and L. D. SCHMIDT, *J. Catalysis*, 1971, **22**, (2), 260-265

The adsorption and absorption of H_2 on Pd

wires was studied using flash filament desorption. The initial H sticking coefficient was 0.13. At 200 K three states, β_1 , β_2 and β_3 , were observed with binding energies of 22, 25 and 35 kcal/mole. At 100 K an α state was observed. The amount of H_2 taken up in the α state greatly exceeds that of the β state; the former probably corresponds to solution of H in Pd.

The Effect of Hydrogen on the Tensile Properties of Palladium

R. J. SMITH and D. A. OTTERSON, *J. Less-common Metals*, 1971, **24**, (4), 419-426

Tensile properties of annealed and non-annealed Pd wire were measured as a function of H content. The yield stress, ultimate tensile stress and elongation at maximum stress showed abrupt changes with respect to H content near phase diagram boundaries. The dependence of tensile properties on H content within a single phase region was interpreted in terms of electronic structure and work hardening.

Magnetic and Electrical Properties of Pd-Rh and Pd-Ag Alloys

I. YA. DEKHTYAR, E. G. MADATOVA and R. G. FEDCHENKO, *Ukr. Fiz. Khim.*, 1971, **16**, (6), 915-921

Magnetic and electrical properties of annealed and deformed Pd-Rh, Pd-Ag and 1 at.% Fe-Pd-Rh alloys were studied. Plastic deformation increases the magnetic susceptibility of alloys with more than 5 at.% Rh, and also increases the electrical resistivity, particularly in binary alloys.

Ordering in PtFe-PdFe and PtFe-PtNi Alloys and Their Magnetic Properties

S. SHIMIZU and E. HASHIMOTO, *J. Japan Inst. Metals*, 1971, **35**, (9), 902-907

Order-disorder transformations in $\text{Pt}_{50-x}\text{Pd}_x\text{Fe}_{50}$ and $\text{Pt}_{50}\text{Fe}_{50-x}\text{Ni}_x$ were studied. Both systems form solid solutions and undergo transformation from disordered f.c.c. to ordered f.c.t. Alloys containing more than 20 at.% Pd show magnetic hardening phenomena and are the most suitable for use as permanent magnetic alloys.

Vapour Pressure of Palladium-based Liquid Alloys

N. A. VATOLIN, A. I. TIMOFEEV and E. L. DUBININ, *Zh. Fiz. Khim.*, 1971, **45**, (8), 2027-2029

The vapour pressures over Pd-Ag, Pd-Cu, Pd-Co, Pd-Ni, Pd-Fe, and Pd-W were measured using the Knudsen effusion method. The thermodynamic activities of the components in the alloys were found.

Study of the Activity of the Components in Some Palladium-based Liquid Metal Alloys by the E.M.F. Method

N. A. VATOLIN, A. I. TIMOFEEV, O. A. ESIN and E. L. DUBININ, *Ibid.*, 2021-2026

The concentration and temperature dependences of e.m.f.s of melts of Pd with Ni, Co, Fe, Cu, Mn and Si were measured. With Ni, Fe, Co and Cu at 1600°C a positive deviation from Raoult's law is observed; a negative one occurs in Pd-Mn and Pd-Si. The two latter alloys show the presence in the melt of ordered groups of compositions close to Pd_xMn_y and PdSi.

On the Magnetic Properties of Powders of Alloys of the System Iron-Palladium

YA. S. SHUR, V. S. BOIDENKO, L. M. MAGAT, G. S. KANDAUROVA and G. M. MAKAROVA, *Fiz. Metal. Metalloved.*, 1971, 32, (3), 562-568

Studies of the magnetic properties and phase compositions of FePd and Fe_{0.7}Pd_{0.3} powders with grain sizes from 3 to 400 μ, previously treated by crushing, annealing and pickling, indicate the mechanism of magnetisation and magnetic reversal in these powders.

On the Composition of the Vapour above Pd-Ba and Pt-Ba Alloys

D. M. CHIZHIKOV, YU. V. TSVETKOV, E. K. KAZENAS, N. P. ESAULOV and V. M. ROZHDESTVENSKII, *Zh. Fiz. Khim.*, 1971, 45, (8), 2064-2065

The composition of the vapours over 2.0 and 22.0 wt.% Ba-Pd at 1515-1720 K and 1.5 wt.% Ba-Pt at 1980 K was investigated by mass spectroscopy. The vapour consists of Ba and BaO. The partial pressures of the components and the rate of vaporisation over 2.0 wt.% Ba-Pd were measured.

Variation of Thermal Expansion Coefficient with the Applied Stress in an Amorphous Metallic Alloy

D. LESEUR, J. Y. THOMAS and V. VENDITTI, *Rev. Phys. Appl.*, 1971, 6, (1), 91-94

The linear thermal expansion coefficient of 20 at.% Si-Pd at 15-100° above ambient increases linearly from 1.95×10^{-5} to 2.08×10^{-5} /deg K for stresses up to 80 kg/mm². Young's modulus is 5300 kg/mm², the temperature coefficient of electrical resistance is 1.20×10^{-4} /deg K and the elastoresistance coefficient is 1.7 ± 0.1 .

The Influence of Transition Metal Additions on the Sintering Behaviour of Tungsten

G. V. SAMSONOV and V. I. YAKOVLEV, *Z. Metallkunde*, 1971, 63, (8), 621-626

The effect of additions of 0.05-1.0 wt.% transition metals, including Pt group metals, on the sintering behaviour of W at 1000-2000°C was studied. The Pt metals promote sintering with the exception of Os, which has no effect. The

activation is probably due to electron exchange between the metals; the free energy is lowered with an increase in d bonds in the system. The sintering diffusion is accelerated by alloying additions for which W acts as an electron donor.

CHEMICAL COMPOUNDS

Thermodynamics of the Gaseous Platinum Oxide PtO₂

I. LAUDER, *J. Chem. Thermodyn.*, 1971, 3, (3), 407-408

The Pt + O₂ system at 1579°C, which contains two oxides, PtO₂ and PtO, is discussed in terms of the Gibbs-Duhem equation.

The Volatilisation and Deposition of Ruthenium Dioxide in Relation to the Fingal Process

M. J. HOLDOWAY, *A.E.R.E. Rept. R-6418*, 1971, (May), 25 pp

The mechanism of Ru volatilisation at high temperatures was studied. Ru transport is due to formation of gaseous RuO₃ and RuO₄ due to O₂ in the system at concentrations > the dissociation pressure of RuO₂. When O₂ is absent or at a lower pressure, RuO₂ dissociates to Ru and O₂ and no Ru is lost. The deposition of RuO₂ was studied using ¹⁰³Ru.

Preparation and Crystal Structure of Osmium Pentafluoride

S. J. MITCHELL and J. H. HOLLOWAY, *J. Chem. Soc., A, Inorg. Phys. Theor.*, 1971, (17), 2789-2794

The preparation of OsF₅ is described. Crystals of the solid are monoclinic, space group P2₁/C with a=5.53, b=9.91, c=12.59 Å, β=99.5°. OsF₅ is isostructural with RuO₅. The structural unit is a tetramer with Os atoms at the corners of a rhombus, linked by binding F atoms.

Crystal Structure of Iridium Trisilicide, IrSi₃

J. G. WHITE and E. F. HOCKINGS, *Inorg. Chem.*, 1971, 10, (9), 1934-1935

Single crystals of IrSi₃ were prepared. The crystals are hexagonal, space group P6₃mc with a=4.351 ± 0.001, c=6.622 ± 0.002 Å and z=2. The structure contains infinite, planar, four-connected layers of Si atoms perpendicular to the c axis with each Ir atom spaced at unequal distances between two Si layers to make equal contacts with Si atoms. The Si-Si distance is 2.175 Å.

Ternary Hydrides of Calcium and Strontium with Iridium, Rhodium and Ruthenium

R. O. MOYER, C. STANITSKI and J. TANAKA, *J. Solid State Chem.*, 1971, 3, (4), 541-549

The ternary hydrides, Ca₂IrH₅, Sr₂IrH₅, Ca₂RhH₅, Sr₂RhH₅ and Sr₂RuH₅ were prepared

by reacting the alkaline earth hydride with a Group VIII metal at high temperature under a H₂ atmosphere. The two metal atoms are arranged in the fluorite structure. The H atoms octahedrally coordinate the Group VIII metal atom; random vacancies of H sites were indicated for the Ir compound.

cis-Dichlorodiammineplatinum(II): Inhibition of Nucleic Acid Synthesis in Lymphocytes Stimulated with Phytohemagglutinin

J. A. HOWLE, H. S. THOMPSON, A. E. STONE and G. R. GALE, *Proc. Soc. Biol. Med.*, 1971, **137**, (3), 820-825

cis-Pt(NH₃)₂Cl₂ inhibited DNA synthesis in human lymphocyte cultures stimulated with phytohemagglutinin. Selectivity was evident at low concentration (3 × 10⁻⁶M). The complex may undergo two sequential transformations, losing Cl⁻ at each step, the resulting species acting bifunctionally to cross-link adjacent nucleophilic centres.

Immunosuppression by Platinum Diammines

M. C. BERENBAUM, *Br. J. Cancer*, 1971, **75**, (9), 208-211

Pt(NH₃)₂Cl₂ and, to a lesser extent, Pt(NH₃)₂Cl₄ inhibit antibody-forming cells in mouse spleen after injection of sheep red cells. The rapidly proliferating cells were most sensitive to the dichloride. The complex acts like an alkylating agent. Pt-en-Cl₂ and Pt-en-Cl₄ were ineffective.

Antitumour and Antimitogenic Properties of cis-Dichloro(dipyridine)platinum(II)

G. R. GALE, J. A. HOWE and E. M. WALKER, *Cancer Res.*, 1971, **31**, (7), 950-952

cis-Pt(py)₂Cl₂ showed less potential antitumour and antimitogenic activity than *cis*-Pt(NH₃)₂Cl₂ but was less toxic to mice. The py complex inhibited the growth of *E. coli* and increased the survival time of mice bearing Ehrlich ascites tumour. In vitro, it also inhibited protein and nucleic acid synthesis by tumours, and DNA synthesis in phytohemagglutinin-stimulated cultures of human lymphocytes.

ELECTROCHEMISTRY

Electrochemical Activity of Electrodeposited and Heat-treated Platinum Electrodes

S. SHIBATA and M. P. SUMINO, *Electrochim. Acta*, 1971, **16**, (9), 1511-1517

The electrochemical activity of a platinised Pt electrode is decreased by annealing in vacuo due to the rearrangement of superficial, metastable Pt atoms to stable lattice positions. The annealed electrode may be activated by oxidation-reduction treatment or by short exposure to air. Activation probably results from the formation of a superficial active monolayer of Pt atoms.

Chemisorption on Platinum and Tungsten

J. M. SALEH, *Trans. Faraday Soc.*, 1971, **67**, (6), 1830-1836.

Adsorption of H₂S, H₂Se, SO₂ and CS₂ on Pt films at -80 to 250°C was studied. Fast dissociation chemisorption of H₂S and H₂Se occurred on Pt films at -80°C. Further slow, dissociating adsorption occurred above 30°C, the activation energies = 46 and 24 kJ/mol respectively. Adsorption of SO₂ and CS₂ was molecular and completely reversible.

ELECTRODEPOSITION AND SURFACE COATINGS

Deposition of Platinum on Teflon and Parylene by Sputtering

M. SONN, G. J. JAKO and W. M. FEIST, *Rev. Sci. Instrum.*, 1971, **42**, (7), 1076-1077

The manufacture of a microelectrode by sputter deposition of Pt on a 0.08-0.13 mm thick film of teflon or parylene is described. The target is a 99.98% pure Pt sheet. Good adhesion of the 1 μ thick Pt coating was obtained.

Photoselective Metal Deposition

D. J. SHARP, *Plating*, 1971, **58**, (8), 786-790

Hydrated SnO₂ is produced when substrates, previously wetted with a dilute SnCl₂ solution, are hydrolysed in water. This layer can be photo-oxidised by a U.V. image and activated by immersion in dilute PdCl₂, thereby depositing Pd on to the unexposed areas. The Pd image catalyses the reduction of metal from electroless plating baths. This method could be used to manufacture printed circuits.

Electrodeposition of Palladium-Cobalt Alloy from Complex Electrolytes with Mixed Ligands

S. N. VINOGRADOV, N. T. KUDRYAVTSEV and G. G. ARTANOVA, *Zashchita Metal.*, 1971, **7**, (5), 612-613

To eliminate the high internal stress of Pd-Co alloys deposited from ammino-chloride complexes Co pyrophosphate was added to the electrolyte. Dense bright fine-crystal deposits of Pd-Co with up to 25% Co and low internal stress were produced using the following electrolyte (g/l): [Pd(NH₃)₄]Cl₂ (on conversion to metal) 13-15; K₄Co(P₂O₇)₂ (on conversion to metal) 13-15; K₄P₂O₇·3H₂O (total) 600-650; NH₄Cl 25-35; NH₄NO₃ 20-30. Recommended conditions are: electrolyte at 35-40°C, pH 9-9.5; current density 0.8-1 A/dm²; insoluble C anode.

Electrodeposition of Osmium

L. GREENSPAN, *Plating in the Electronics Industry - Third Symposium of American Electroplaters Society Inc.*, 1971, (Feb 3-4), 221-229

The electrodeposition of Os from an alkaline solution of osmic acid containing conducting

salts is described. The deposits are bright up to 50 μm thick, and have excellent adhesion. A study of the use of Os-plated reeds for reed switches shows that Os is superior to Rh.

LABORATORY APPARATUS AND TECHNIQUE

Use of the Macroprobe for the Study of a Corroded Platinum Crucible

M. GRASSERBAUER, *Microchim. Acta*, 1971, (2), 335-340

The macroprobe, an X-ray analyser with electron beam excitation, was used to study corroded Pt crucibles. The pits in the corroded crucible consisted of a Pt-Si alloy; the development of pit-forming corrosion sites and the formation of cracks is discussed.

JOINING

Strength Behaviour of Vacuum-brazed Creep-resistant Materials

H. LANGE, *Schweissen Schneiden*, 1971, 23, (1), 14-17

Samples of heat resisting alloys of type Ni-Cr-Ti-Al were vacuum brazed with filler metals including 21%Pd-31%Mn-Ni and 40% Ni-Pd. The tensile strength decreased with increasing temperature for all brazed joints except those with Pd-Mn-Ni.

HETEROGENEOUS CATALYSIS

Nitric Acid Development Aims at Cutting Pollution and Catalyst Loss

D. J. NEWMAN and B. J. HULBERT, *Eur. Chem. News Large Plants Supp.*, 1971, (Sept. 24), 26, 28, 30, 32, 36

Methods for the reduction of Pt loss from catalysts for NH_3 oxidation plants are described; they include filters and Pd-Au "getter" gauzes. Catalysts for the combustion of pollutants from HNO_3 manufacture, such as Pt or Pd on wire, Al_2O_3 pellets or honeycombs are described.

Hydrogenation of Cyclohexene, *cis*-Cyclononene and *cis*-Cyclododecene over Pt Black

E. S. BALENKOVA, V. I. ALEKSEEVA and S. I. KHRMOV, *Neftekhimiya*, 1971, 11, (4), 483-486

Liquid-phase hydrogenations of cyclohexene, *cis*-cyclononene and *cis*-cyclododecene over Pt black were studied at 21-75°C. The rate of hydrogenation varied with ring size.

Transannular Dehydrocyclisation of Dimethylcyclooctanes

V. M. MAKUSHINA, O. A. AREF'EV and A. A. PETROV, *Neftekhimiya*, 1971, 11, (4), 528-532

The reactions of 1,2-, 1,3-, 1,4-, and 1,5-di-

methylcyclooctanes over Pt catalysts were studied at 260-300°C. The chief reaction is transannular dehydrocyclisation to form the respective dimethylbicyclo-[3.3.0]-octanes.

The Effect of Heat Treatment on the Catalytic Properties of Platinum Adsorption Catalysts

ZH. V. STREL'NIKOVA and L. E. MARTYSHKINA, *Vest. Moskov. Univ., Ser. II, Khim.*, 1971, (4), 486-488

Heat treatment of Pt adsorption catalysts does not affect the composition of the active centre, but changes the magnitude of the absorptive capacity.

On the Distribution of Hydrogen Adsorbed from Solutions on the Surface of Some Hydrogenation Catalysts. III. Effect of Mercury Poisoning on the Form of the Differential Isotherms of Hydrogen Adsorption on Platinum

YU. A. PODVYAZKIN, O. R. SERGUTKINA and N. A. DUGIN, *Kinet. Kataliz*, 1971, 12, (4), 1068-1070

The effect of Hg poisoning of Pt for 2, 10 and 40% surface coverage and 0-40°C on the form of the differential isotherm of H_2 adsorption is caused by Hg displacing H_2 bonded to the Pt.

Physical and Chemical Characterisation of Platinum-Rhodium Gauze Catalysts

L. D. SCHMIDT and D. LUSS, *J. Catalysis*, 1971, 22, (2), 269-279

10% Rh-Pt gauze catalysts for NH_3 oxidation and HCN production were studied using scanning electron microscopy, Auger spectroscopy and sputtering techniques. Normal activation produced surface area increases and the formation of randomly oriented facets. Catalysts treated with H_2S for higher activity showed crystalline surfaces consisting predominantly of (100) planes. The gauze wires were permeated by rectangular-shaped channels $\sim 3 \mu$ in width.

Effect of Chlorine and Water on Benzene Reforming on a Platinum Catalyst

O. SVAJEL, *Chem. Prumysl*, 1971, 21, (7), 315-319

Pt/ Al_2O_3 catalysts for C_6H_6 reforming contained 0.1-1.2 wt.% Cl, the optimum concentration being 0.3-0.7 wt.%. Lower concentrations decrease the dehydrocyclisation reaction so that low octane petrol is formed. Higher concentrations show hydrocracking properties and are unstable.

Peculiar Effect of Hydrogen Pressure and Adsorption of Water on the Activity of Platinum/Alumina Catalysts in the Hydrogenolysis of Methylcyclopentane

I. I. LEVITSKII, KH. M. MINACHEV and E. A. UDAL'TAOVA, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1971, (9), 1913-1917

Studies of the effects of p_{H_2} and H_2O adsorption

on the activity of 0.3% Pt/Al₂O₃ in the hydrogenolysis of methylcyclopentane showed that, as p_{H₂} increased from 9 to 49 atm, catalyst activity decreased when the catalyst contained adsorbed H₂O but rose when the catalyst was free of H₂O. Activity also decreased during the elimination of H₂O from the catalyst at a total pressure of 10 atm but rose during the same process at 50 atm total pressure. Two mechanisms form the basis of the changes in opposite directions of catalytic activity as p_{H₂} increases or as H₂ adsorption decreases.

Effect of Rare-earth Elements on Activity of Aluminoplatinum Catalysts

N. S. KOZLOV, V. A. POLIKARPOV and G. M. SEN'KOV, *Vestsi Akad. Navuk Belaruss. S.S.R., Ser. Khim. Navuk*, 1971, (2), 110-114

Addition of 0.1-1% Ce, Nd, Y, Gd or Yb improves the catalytic activity of Pt/Al₂O₃ for C₈H₁₄ conversion. The yield of cracking products is reduced, and the yield of isomers increased at 400-450°C; the cyclisation activity is unchanged.

Aromatisation of 2-Methylheptane and 2,4-Dimethylhexane in the Presence of Platinum/Alumina Catalyst in Pulsed Conditions

V. G. VLASOV, YU. V. FOMICHEV and B. A. KAZANSKII, *Neftekhimiya*, 1971, 11, (4), 510-516

The aromatisation of 2-methylheptane and of 2,4-dimethylhexane in the presence of 0.6% Pt/γ-Al₂O₃ and 0.6%Pt+0.8%Na₂O/Al₂O₃ was studied. C₈-dehydrocyclisation occurs during aromatisation. Introduction of Na₂O reduces the yield of C₈ aromatics and decreases the amount of isomers. Aromatisation probably occurs by C₈-dehydrocyclisation.

On the Effect of Sulphurisation on the Activity of Platinum/Alumina Catalysts

G. N. MASLYANSKII, B. B. ZHARKOV, A. Z. RUBINOV and T. M. KLIMENKO, *Kinet. Kataliz*, 1971, 12, (4), 1060-1061

S added to Pt/Al₂O₃ in one or another stage reduces the activity of the catalyst for C₆H₆ hydrogenation but increases its thermal stability. The treated catalyst has maximum activity for reduction at 800°C.

Effect of the Nature of the Initial Platinum-containing Compounds on the Properties of Platinum/Alumina Catalysts for Aromatisation of Hydrocarbons

S. B. KOGAN, T. S. KISELEVA and N. R. BURSIIAN, *Ibid*, (5), 1338-1341

Pt/Al₂O₃ catalysts prepared from various Pt(IV) ammoniates and from H₂PtCl₆ (0.6 wt.% Pt) were tested in aromatisations of n-C₆H₁₄, cyclohexane and methylcyclopentane, and in decomposition of H₂O₂. The concentration of Pt ions was determined. The catalyst activity in

n-C₆H₁₄ aromatisation depended on the nature of the initial Pt compound. Those based on mono- and dichloroamino complexes had the greatest activity. No analogous maximum activities were observed in the other reactions. An explanation of this effect is given.

Vapour-phase Catalytic Synthesis of Xylenes from Toluene and Formaldehyde

M. OKADA, Y. ASAMI, Y. KAKU and K. UOYA, *Sekiyu Gakkai Shi*, 1971, 14, (2), 113-118

The vapour phase synthesis of xylenes from PhCH₃ and HCHO in the presence of H₂ was studied over various catalysts. 1 wt.% Pt/SiO₂-Al₂O₃ catalyst was the most selective for producing p-xylenes. The stability of this catalyst was greater than that of SiO₂-Al₂O₃.

Investigation of Mixed Platinum Group Metal Catalysts on Supports for the Reduction of Nitro Compounds

N. I. POPOV, D. V. SOKOL'SKII, F. B. BIZHANOV and V. F. PECHENKINA, *Zh. Fiz. Khim.*, 1971, 45, (10), 2637-2640

Studies of activity of binary supported Pt group metal catalysts during hydrogenations of o-nitroanisole and nitrobenzene showed that significantly increased activity is connected with an increase in the rate of production of active components on their surfaces.

Kinetics and Mechanism of the Oxidation of Carbon Monoxide on Pure Palladium

I. I. TRET'YAKOV, A. V. SKLYAROV and B. R. SHUB, *Kinet. Kataliz*, 1971, 12, (4), 996-1002

Oxidation of CO by O₂ on Pd in 10⁻⁶-10⁻¹ torr vacuum at 80-500°C proceeds by gas phase reaction of adsorbed O with CO. The reaction is retarded where the gases are present in excess amounts because there is concurrent chemisorption of O and O₂.

Kinetics of Dehydrogenation of Cyclohexane on Palladium Foil

V. M. GRYAZNOV, L. F. PAVLOVA, P. RIVERA, A. ROSEN and E. KHAURES, *Ibid*, (5), 1197-1202

Studies of the kinetics of the dehydrogenation of cyclohexane in C₆H₆ on Pd foil at 250-322°C, p_{H₂} = 0-500 mm Hg, p_{C₆H₁₂} = 10-100 mm Hg show that the reaction rate rises as p_{H₂} and p_{C₆H₁₂} increase. The kinetic equation is derived and is related to the reaction mechanism. The apparent activation energy is calculated from the temperature dependence of the reaction rate.

Hydrogenation of Nitrobenzene over Palladium-Silver Catalysts

A. METCALFE and M. W. ROWDEN, *J. Catalysis*, 1971, 22, (1), 30-34

The rates of hydrogenation of nitrobenzene in n-butanol were measured over Pd-Ag alloy catalysts. The activation energy varied from ~5 kcal/

mole on Pd-rich alloys to ~25 kcal/mole on Ag-rich alloys. This is consistent with the theory that promotion of electrons from within the conduction band to the Fermi surface of the solid is rate determining.

Dehydrocyclisation of Alkenes and of Alkadienes in the Presence of Palladium/Alumina Catalyst

V. S. FADEEV, I. V. GOSTUNSKAYA and B. A. KAZANSKII, *Neftekhimiya*, 1971, 11, (4), 523-527
The aromatisation of 1-hexene, hexa-1,5-diene, hexa-2,4-diene and methylcyclopentane and 1-methylcyclopentene-2 over Pd/Al₂O₃ was studied. The degree of aromatisation increases with the degree of unsaturation of the olefin, and for hexene and hexadiene is greater in He than in H₂.

Exchange with Deuterium of Some Cyclic Hydrocarbons Catalysed by Palladium

H. A. QUINN, J. H. GRAHAM, M. A. MCKERVEY and J. J. ROONEY, *J. Catalysis*, 1971, 22, (1), 35-40
The isotopic D/H exchange in cyclic hydrocarbons catalysed by Pd was investigated. Pd/SiO₂ and Pd films were used. The results indicate that the exchange proceeds via roll-over of intermediate olefins.

The Structure and Activity of Supported Metal Catalysts. VI. Measurement of Dispersion in Palladium-Charcoal Catalysts

D. POPE, W. L. SMITH, M. J. EASTLAKE and R. L. MOSS, *J. Catalysis*, 1971, 22, (1), 72-84

The metal dispersion in Pd/C catalysts was estimated from X-ray line broadening and intensity measurements, as this method avoids surface cleaning. The mildest surface cleaning can induce sintering, but the extent is minimised at low Pd content and uniform Pd distribution. The feasibility of using CO chemisorption as a measure of Pd area is discussed.

A Study of the Active Site of the Catalyst Composed of Palladium and Active Charcoal

K. FUJIMOTO, T. TAKAHASHI, Y. NEGAMI and T. KUNUGI, *Kogyo Kagaku Zasshi*, 1971, 74, (6), 1076-1080

A deactivated Pd salt/C catalyst was reactivated by HCl so that C₂H₄ oxidation gave four times the amount of acetaldehyde produced using the deactivated catalyst. When O₂ was added the catalytic activity increased to 70-80 % standard activity. Surface oxides on the active C are not effective for the reoxidation of Pd.

The Effect of Alkali Additions on the Properties of Palladium/Polyacrylonitrile Catalysts

O. A. TYURENKOVA and L. A. CHIMAROVA, *Zh. Fiz. Khim.*, 1971, 45, (9), 2216-2219

Small additions of alkali to Pd/polyacrylonitrile

increase its activity in hydrogenation of dimethyl-ethynylcarbinols. The maximum rate of reaction occurs when Pd:KOH = 1:0.39. The 39% added alkali arises from the need to convert all Pd to Pd(OH)₂. Further addition of KOH leads to a less active catalyst.

Stereospecific Hydrogenations. V. Hydrogenation Rates Using Palladium-on-Poly-S-leucine and Palladium-on-Poly-S-valine

R. L. BEAMER and W. D. BROWN, *J. Pharm. Sci.*, 1971, 60, (4), 583-588

Hydrogenations of α -methylcinnamic acid and α -acetamidocinnamic acid were more rapid on Pd/poly-S-leucine (helical catalyst) than on Pd/poly-S-valine (non-helical catalyst). The reactants occupy different sites on the catalyst surface. Inhibition studies were carried out, from which mechanisms are proposed.

Hydrogenation of Fatty Acids from Cottonseed Oil

K. K. DOMANSKAYA, A. I. GLUSHENKOVA and A. L. MARKMAN, *Maslo-Zhir. Prom.*, 1971, 37, (4), 23-26

Hydrogenation of fatty acids on a supported Pd catalyst followed a zero order reaction relative to the acids. Isomerisation took place, forming conjugated systems in linoleic acids.

Catalytic Oxidation. III. The Mechanism of Ethylene and Propylene Oxidation over Supported Rhodium and Ruthenium

N. W. CANT and W. K. HALL, *J. Catalysis*, 1971, 22, (3), 310-323

The kinetics of C₂H₄ and C₃H₆ oxidation over Rh/ α -Al₂O₃ and Ru/ α -Al₂O₃ are similar to those over SiO₂-supported Rh and Ru. Substitution of D for H in the CH₃ group reduced the rate of C₃H₆ oxidation over Rh, showing that H abstraction is rate determining. The mechanisms for acetone and acrolein production are given.

On the Asymmetric Hydrogenation of Carbonyl Groups in the Presence of Modified Ruthenium Catalysts

E. I. KLABUNOVSKII, N. P. SOKOLOVA, A. A. VEDENYAPIN and YU. M. TALANOV, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1971, (8), 1803-1804

Optically active (-)- β -oxybutyrate was produced by hydrogenation of acetoacetic esters over Ru/SiO₂ modified by D-tartaric acid at pH 4.2-5.9. The greatest asymmetric yield occurred at pH 5.5.

The Unique Double-bond Isomerisation Properties of a Ruthenium Oxide-Silica Catalyst

L. F. HECKELSBERG and R. L. BANKS, *J. Catalysis*, 1971, 22, (2), 284-286

RuO₂/SiO₂ catalyses the isomerisation of 1-butene to 2-butene, the ratio of *trans*- to *cis*-2-butene

produced being 3-5:1. Other catalysts give more of the *cis*-isomer. The *cis*-isomer probably forms a stable complex with Ru that does not readily react or desorb.

Hydrogenation of Butynediol on Metal Catalysts of the Platinum Group

D. V. SOKOL'SKII, A. M. PAK and E. I. TEN, *Izv. Akad. Nauk Kaz. S.S.R., Ser. Khim.*, 1971, 21, (2), 71-73

Hydrogenation of butynediol on Pt, Pd and Os blacks and on Pt-Os and Pd-Os catalysts in EtOH was studied, together with the effect of BuNH₂ and 24% aqueous NH₃ additions on the mechanism. Os black had a very low activity. Hydrogenolysis took place on Pt-Os. Increasing the temperature from 20 to 40°C decreased the reaction rate and addition of NH₃ and BuNH₂ stopped the hydrogenation, but increased the selectivity on Pd-Os and Pd black respectively.

Liquid Phase Hydrogenation of Cycloolefins

E. S. BALENKOVA, V. I. ALEKSEVA and S. I. KHROMOV, *Kinet. Kataliz*, 1971, 12, (5), 1224-1229

Studies of liquid-phase hydrogenations of cycloolefins over Pt, Ir, Pd, and Rh blacks at 1 atm and various temperatures showed that the rate constants of the reactions decrease from cyclohexane to *cis*-cyclodecene and rise again for *cis*-cyclododecene.

Hydrogenolysis and Isomerisation of *n*-Pentane on Group VIII Transition Metals

E. KIKUCHI, M. TSURUMI and Y. MORITA, *J. Catalysis*, 1971, 22, (2), 226-236

The reaction of *n*-C₅H₁₂ with H₂ was studied over Pt metal catalysts. The specific activity for hydrogenolysis was in the order Ru > Rh > Pt > Ir > Pd. On Ru, Rh and Ir multiple bond breaking occurred at low H₂ partial pressure. On Pd and Pt single C-C bond cleavage occurred. Pt and Pd are also active for isomerisation of *n*-C₅H₁₂ to *iso*-C₅H₁₂, the activity of Pt decreasing with increasing H₂ partial pressure.

The Electrical Conductivity of Supported Metal Catalysts

S. J. THOMSON and G. A. HARVEY, *Ibid.*, (3), 359-363
Studies of the electrical conductivity of Rh, Pt, Ru and Pd on Al₂O₃ and SiO₂ show that these systems are semiconducting, and are electronic or protonic in nature. At 50-350°C activation energies for conduction are 8-27 kcal/mole.

HOMOGENEOUS CATALYSIS

Dimerisation of Conjugated Dienes Using Palladium(II) Compounds

T. ARAKAWA and H. MIYAKE, *Kogyo Kagaku Zasshi*, 1971, 74, (6), 1143-1149

Catalytic activation of diene dimerisation catalysts

such as Pd(II) acetoacetate, ditertiarybutoxy-Pd(II) and Pd(II) acetate was studied. The dimerisation is probably due to reduction of Pd by dienes and added olefins followed by diene coordination and protonation.

Catalysis by Palladium Salts. I. The Role of Dimethylformamide and Related Solvents in the Palladium-Olefin Interaction

F. CONTI, M. DONATI, G. F. PREGAGLIA and R. UGO, *J. Organomet. Chem.*, 1971, 30, (3), 421-429

The synthesis of π -allylPd(II) compounds [PdCl(C_nH_{2n-1})]₂ from olefins and PdCl₂ under mild conditions is described. The reaction mechanism and solvent effects are discussed with reference to the catalytic activity of Pd(II) salts in non-aqueous solvents. The behaviour of PtCl₂ under similar conditions is compared with that of PdCl₂.

Palladium-catalysed Reactions of 1,3-Dienes with Active Methylene Compounds. II.

G. HATA, K. TAKAHASHI and A. MIYAKE, *J. Org. Chem.*, 1971, 36, (15), 2116-2123

1,3-dienes react with active methylene and methyne compounds in the presence of Pd and Pt complexes to form the corresponding 2,7-alkadienyl derivatives. In Pd-catalysed reactions of 1,3-butadiene, 1,2- and 1,4-adducts are the main products; with Pt complexes the branched 1,2-adduct is the main product. A reaction system is postulated.

The Selectivity of Polymer Supported Homogeneous Catalysts

R. H. GRUBBS and L. C. KROLL, *Abstr. Papers, 162nd Natl. Mtg., Am. Chem. Soc.*, 1971, (Sept), POLY 68

RhCl(PPh₃)₃ was attached to 2% divinylbenzenestyrene copolymer beads by a phosphate link. The supported complex catalysed reduction of olefins at a different rate from the non-supported complex. A graph of molecular size/log relative rate shows a linear relationship, suggesting that the reduction occurs inside the polymer beads and that solvent channels in the polymer restrict the entrance of the olefins to the catalytic site.

Mechanism of Osmium Tetroxide Catalysed Oxidation of Acetaldehyde with Ferricyanide

P. C. PANDEY, V. N. SINGH and M. P. SINGH, *Indian J. Chem.*, 1971, 9, (5), 430-431

The kinetic studies indicated an oxidation involving enolisation as the rate determining step, followed by formation of an Os(VIII)-enolate complex which rapidly decomposes to Os(VI)O₂(OH)₄²⁻ and the intermediate oxidation product. The Os(VI) species is rapidly oxidised to Os(VIII)O₄(OH)₃³⁻ with ferricyanide. Oxalate ions were the final oxidation product.

Kinetics and Mechanism of the Reaction of Hydrogen and of the Homogeneous Catalytic Hydrogenation of Ethylene with Hydrido-carbonyltris(triphenylphosphine)iridium(I)

M. G. BURNETT and R. J. MORRISON, *J. Chem. Soc., A, Inorg. Phys. Theor.*, 1971, (14), 2325-2330

The kinetics of the reaction of H_2 with $IrH(CO)(PPh_3)_3$ were studied, and rate constants for the two step formation of $IrH_3(CO)(PPh_3)_2$ were found. Kinetics for the hydrogenation of C_2H_4 in the presence of this complex are given. The results suggest that $IrH(CO)(PPh_3)_2$ is the active catalyst for this reaction.

Transition Metal Complexes as Selective Isomerisation Catalysts. Preparation of Compounds Having an Exocyclic Double Bond

J. E. LYONS, *J. Org. Chem.*, 1971, 36, (17), 2497-2505

The isomerisation of vinylcycloalkenes and -alkanes to compounds with exocyclic double bonds was studied using $RuCl_2(PPh_3)_3$, $PtCl_2(PPh_3)_3$ and $SnCl_2$ under H_2 pressure, and $IrCl(CO)(PPh_3)_2$. The reactions are very selective in retaining the double bond. The Ru(II) complex exhibits catalytic activity only in the presence of air or hydro-peroxides as it forms a CO complex which has the high catalytic activity.

FUEL CELLS AND BATTERIES

High-stability Cathodes for Fuel Batteries

D. C. CONSTABLE, *J. Electrochem. Soc.*, 1971, 118, (8), 1391-1393

The production of stable cathodes for use in fuel cells with acid electrolyte and soluble organic fuel is described. A high Pt loading improves the cathodes' stability. Electrodes prepared from Pt and PTFE show stable performance with a PTFE content of 2.8-6.7 mg/cm². Those on graphited substrates show inferior stability.

GLASS TECHNOLOGY

Melting of Optical Glasses in a Platinum Crucible

J. HONZU, *SklarKeram.*, 1971, 21, (4), 97-98

Superior quality optical crown glasses were produced by induction melting of stirred high purity glass components in a 50l Pt crucible.

Oxidation States and Stereochemistry of Some Platinum Group Metals in Sulphate and Bisulphate Melts and Glasses

J. A. DUFFY and W. J. D. MACDONALD, *Phys. Chem. Glass.*, 1971, 12, (3), 87-90

Of the six Pt metals, Rh, Pd and Pt have the simplest chemistry in molten $NaHSO_4$ - $KHSO_4$ and molten K_2SO_4 - $ZnSO_4$. The crystal field and

charge transfer spectra indicate that the stable states are Rh(III), Pd(II) and Pt(IV), and that these exist as sulphato complexes. Rh(III) and Pt(IV) are octahedrally coordinated; Pd(II) coordination is between octahedral and square planar.

Oxidation States of Ruthenium in Glasses

J. MUKERJI and S. R. LISWAS, *Glass Technol.*, 1971, 12, (4), 107-111

Oxidation states of Ru in silicate and phosphate glasses were found by spectrophotometric studies. In silicates Ru(IV) is in equilibrium with Ru(III) in acidic glasses (>25 mol% Na_2O); Ru(VI) and (IV) were found in basic glasses. Only Ru(VII) is found in phosphate glasses containing less than 50 mol% P_2O_5 , Ru(VIII) with higher concentrations. Only tetracoordinated Ru(VI) can be accommodated to any extent in both types of glass.

ELECTRICAL AND ELECTRONIC ENGINEERING

Polymolecular Adsorption of Barium Oxide on a Platinum Substrate

A. R. SHUL'MAN, T. S. KIRSANOVA, L. P. KARPOVA and V. M. BELOVA, *Zh. Fiz. Khim.*, 1971, 45, (9), 2288-2291

Studies on the evaporation of BaO films dusted on a Pt band showed that initial heating to 1140-1270 K was probably accompanied by crystallisation. As the layer thickened from 1.3-2.2 monomolecular layers the rate of evaporation rose and the heat of vaporisation fell; from 2.5-5.2 layers the rate of evaporation fell and the heat of vaporisation rose.

Plastic Encapsulated Transistors

C. F. MAGUIRE, F. J. KOONS and Q. T. JARRETT, *Solid State Technol.*, 1971, 14, (8), 37-43

pnp semiconductor chips are made by coating SiNi-covered wafers with Pt and heating to form PtSi in the contact windows. After removal of excess Pt, layers of Ti and Pt are sputtered sequentially. Photoresist is used to mask non-contact areas, thus enabling a final layer of gold to be plated on to the contact area. The pnp chips are used in the manufacture of plastic encapsulated transistors.

TEMPERATURE MEASUREMENT

An Intercomparison of High Temperature Platinum Resistance Thermometer and Standard Thermocouples

J. P. EVANS and S. D. WOOD, *Metrologia*, 1971, 7, (3), 108-130

Nine Pt resistance thermometers and eight

Pt:10% Rh-Pt thermocouples were compared at 50°C intervals from 630.74–1064.43°C. The standard deviation with the resistance thermometers was ≈ 4 mK, and 25–30 mK with the thermocouples. Values on IPTS-68 could be determined with a single thermometer with one-third of the uncertainty of a single thermocouple. If a practical temperature scale were redefined using Pt resistance thermometers it could be realised with less uncertainty than IPTS-68.

Effect of Pressure on the Thermal E.M.F. of the Platinum/Platinum-10 per cent Rhodium Thermocouple

P. M. BELL, F. R. BOYD and J. L. ENGLAND, *Nat. Bur. Stds. Spec. Publ. 326*, (Mar.), 63–65

The effect of pressure on the e.m.f. of a Pt:10% Rh-Pt thermocouple was measured. Pressure decreases the thermal e.m.f., so that a positive correction to the thermocouple reading is required at pressures above atmospheric. The effect increases non-linearly with temperature and pressure. The maximum effect was 20 μ V at 509°C and 3.5 kbar corresponding to an apparent correction of 2°C.

Effect of Pressure on the E.M.F. of Thermocouples

I. C. GETTING and G. C. KENNEDY, *Ibid.*, 77–80

If the temperature of a thermocouple junction at high pressure is different to that where the elements emerge into a low pressure environment, substantial effects on the thermal e.m.f. are observed. Measurements on Pt and 10% Rh-Pt single wire are used to formulate a correction graph for Pt: 10% Rh-Pt thermocouple readings under these conditions.

Temperature Measurement by Thermal Noise at High Pressures

R. H. WENTORF, *Ibid.*, 81–89

The temperature of a small C resistor (700–3000 ohm) in a high pressure cell next to a Pt: 10% Rh-Pt thermocouple was measured by thermal noise. Runs were made at 40 and 50 kbar up to 1,400 K. At high temperatures the thermocouple indicated a temperature 40–60 K too low, in fairly good agreement with estimates made by other methods.

Sensor-lance for BOF Control

D. W. KERN, P. D. STELTS and R. J. FRADENECK, *J. Metals*, 1971, 23, (8), 9–19

A sensor-lance for monitoring turndown C and temperature is being used at Bethlehem Steel's basic oxygen furnace shop. The sensors contain Pt:10%Rh-Pt or 6%Rh-Pt:30%Rh-Pt thermocouples. Use of this system has increased the accuracy of turndown C and temperature control, doubled the heats ready to tap at first turndown and decreased the heat time.

Amorphous Alloy Resistance Thermometer Development

C. R. TALLMAN, *Adv. Instrumentation (Proc. 25th Ann. I.S.A. Conf.)*, 1970, 25, (2), paper 619, 6 pp

A unique resistance thermometer with enhanced sensitivity at cryogenic temperatures is described. It uses an amorphous 7%Cr-20%Si-Pd alloy whose resistivity is greatest at 4 K, and decreases with increasing temperature up to 600 K. The sensitivity is greater than that of Pt below 20 K. The thermometer was developed for use in a nuclear environment; the design concepts, theory and results are discussed.

NEW PATENTS

METALS AND ALLOYS

Permanent Magnetic Alloy

CITIZEN WATCH CO. LTD. *U.S. Patent 3,591,373*
A permanent magnetic alloy contains 15–40 at.% Pt, 5–35 at.% Au and 40 at.% Fe.

Dispersion Strengthened Metals

JOHNSON MATTHEY & CO. LTD.
German Offen. 2,102,980 Dutch Appl. 71.00,842
Au, Ag and Pt metals and their alloys are hardened by internal oxidation of an additive such as Zr. After addition of Zr the alloy is powdered, cold worked and exposed to a gas which converts the Zr to a stable refractory oxide, ZrO₂. The product is compacted and sintered.

CHEMICAL COMPOUNDS

Rhodium Complexes

BRITISH PETROLEUM CO. LTD.
British Patent 1,249,303

In the manufacture of Rh complexes, a Rh carbonyl carboxylate is reacted with a reagent (containing at least one active H atom) which is either a β -diketone or a Schiff base of a β -diketone. This gives a complex of the type Rh(CO)₂acac.

ELECTROCHEMISTRY

Hydroquinone Production

K. DURKES *German Offen. 1,953,951*
The electrochemical oxidation of C₆H₆ to hydro-