

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Vapour Pressure and Heat of Sublimation of Platinum

E. R. PLANTE, A. B. SESSOMS and K. R. FITCH, *J. Res. NBS, Pt. A, Phys. Chem.*, 1970, **74A**, (5), 647-653

The vapour pressure of Pt was measured by the Langmuir method at 1700-2000K and the results are tabulated. The mean value of the third law heat of sublimation is 564.49 ± 2.1 kJ/mol, but second law values tended to be lower due to experimental error.

Photoelectric Determination of the Work Function of Gold-Platinum Alloys

R. BOUWMAN and W. H. M. SACHTLER, *J. Catalysis*, 1970, **19**, (2), 127-140

Films of Pt, Au and their alloys were prepared by vapour deposition. The photoelectric emission of these films was investigated. Equilibrated alloys of compositions within the miscibility gap of the Pt-Au phase diagram possessed identical work functions. This result agrees with the expectation that the Au-rich alloy envelops crystallites of the coexisting Pt-rich alloy. CO causes an enrichment of the Pt in the surface.

Ordering in Fe-Pt Alloys

E. N. VLASOVA and T. P. SAPOZHKOVA, *Fiz. Metal. Metalloved.*, 1970, **30**, (5), 980-985

X-ray studies of the ordering of monocrystalline 32 at.% Pt-Fe during isothermal annealing at 750°C indicated initial formation of a metastable homogeneous structure succeeded by separation into two ordered phases FePt and Fe₃Pt.

Resistive Behaviour of Dilute PdFe Alloys about the Curie Temperature

M. P. KAWATRA, J. I. BUDNICK and J. A. MYDOSHI, *Phys. Rev. B.*, 1970, **2**, (6), 1587-1592

The behaviour of the magnetic part of the electrical resistivity ρ_m of 0.1-1.0 at.% Fe-Pd near the Curie temperature was analysed. The ferromagnetic critical temperature was determined from the location of the maximum in $d\rho_m/dT$, and varies with concentration as C^n , where $n = 1.65 \pm 0.05$.

Thermodynamic Properties of Solid Nickel-Platinum Alloys

R. A. WALKER and J. B. DARBY, *Acta Metall.*, 1970, **18**, (12), 1261-1266

The activities and free energies of solid Ni-Pt

alloys at 1625 K were calculated from vapour-pressure measurements. Heats of formation at 298 K were measured by liquid Sn solution calorimetry. The results reflect the ordered structures that exist at low temperatures in the Ni-Pt system.

Magnetic Investigations of the Isoelectronic Palladium-Platinum System

W. TREUTMAN, *Z. Angew. Phys.*, 1970, **30**, (1), 5-8

The magnetic susceptibility of Pd-Pt was measured at 14-800 K, and shows a sharp increase with increasing Pt concentration. New electronic band and density of states calculations are presented, and $\chi(O,c)$ results for the Pd-Pt system are discussed in terms of these and the Stoner-Wohlfarth enhancement formula.

Thermal Stability and Structure of the 7% Rh-Pt Alloy in Relation to Prior Deformation

E. I. RYTVIN and L. A. MEDOVYI, *Metalloved. Term. Obrabot. Metal.*, 1970, (11), 53-55

The amount of deformation of an annealed 7% Rh-Pt alloy affects its structure and the rate of creep. At 1400°C the minimum resistance to creep corresponds to 15% deformation; at 1200°C to 8% deformation.

Electrical and Tensile Properties of Cu-ThO₂, Au-ThO₂, Pt-ThO₂ and Au-Al₂O₃, Pt-Al₂O₃

N. FUSCHILLO and M. L. GIMPL, *J. Mater. Sci.*, 1970, **5**, (12), 1078-1086

Dispersion-strengthened alloys of Pt, Au and Cu containing ThO₂ and Al₂O₃ were prepared by precipitating the elements from a solution containing a suspension of the oxide phase. Alloys containing <2 vol.% oxide phase could be made into wire. Tensile strength, elongation, hardness and resistivity were measured as a function of temperature up to 1000°C. The alloys exhibit high conductivity and superior strength, hardness and oxidation resistance at high temperatures.

Thermal Expansion of Rhodium, Iridium and Palladium at Low Temperatures

G. K. WHITE and A. T. PAWLOWICZ, *J. Low Temp. Phys.*, 1970, **2**, (5-6), 631-639

Coefficients (α) of linear thermal expansion of Rh, Ir and Pd are 8.45, 6.65 and $11.78 \times 10^6/\text{deg K}$ at 283K and 3.50, 3.43 and $6.21 \times 10^6/\text{deg K}$ at 75K. At temperatures below 10K α may be represented by

$$10^{10}\alpha = 20T + 0.052T^3 \text{ (Rh)}$$

$$10^{10}\alpha = 9T + 0.070T^3 \text{ (Ir)}$$

$$10^{10}\alpha = 40.5T + 0.435T^3 \text{ (Pd)}$$

The T and T^3 terms are identifiable with electron and lattice vibrational components.

New Data Concerning the Migration of Hydrogen and Deuterium Dissolved in Palladium under the Action of an Electric Field

A. HEROLD and J.-G. RAT, *C. R., Sér. C*, 1970, **271**, (13), 701-704

The previously described migration of H_2 and D_2 dissolved in a Pd wire under the action of a continuous current cannot be reproduced in the presence of traces of hydrocarbons. The mobilities obtained from the flow of the transported gas are less than those calculated using thermal diffusion coefficients, which indicates an incomplete ionisation of the dissolved atoms.

Note on the Debye Temperature of Palladium

J. S. BROWN, *J. Phys. C, Solid State Phys.*, 1970, **3**, (9), L175-L177

A comparison of the values of the Debye temperature for f.c.c. Pd is given for several different model calculations, and a correlation with various experimental results is discussed.

Study of the Diffusion of Hydrogen in Pd and Pd-Ag Alloys with a Pulse Method

H. ZÜCHNER, *Z. Naturf. A*, 1970, **25**, (10), 1490-1496

Diffusion coefficients of H_2 in Pd and Pd-Ag alloys were determined at low H_2 concentration and 0-60°C by an electrochemical pulse method. The pre-exponential factor D_0 decreases slightly with rising Ag content. The energy of activation depends on the Ag content, going through a minimum at $\approx 15\%$ Ag.

I. Study of the Adsorption of Hydrogen on Filaments of Pure Palladium

B. TARDY and S. J. TEICHNER, *J. Chim. Phys.*, 1970, **67**, (11-12), 1962-1967

The adsorption of H_2 on evacuated Pd filaments was studied by flash desorption. The desorption curves are complex due to impurities (CO and H_2O) which are also desorbed. Gas analysis shows adsorption of a single species of H_2 on Pd in an amount less than the value corresponding to a monolayer.

II. Adsorption of Hydrogen on a Series of Gold-Palladium Alloys

Ibid., 1968-1972

The adsorption of H_2 on Au-Pd alloy filaments was studied. The amount of H_2 adsorbed increases with the Au content up to 30%, then decreases when the Au content is 50%. The latter value corresponds to complete filling of the d orbitals of Pd.

Investigation of the Pd-Ba Composition Diagram

E. M. SAVITSKII, V. P. POLYAKOVA and E. M. KHORLIN, *Izv. Akad. Nauk S.S.S.R., Metall.*, 1970, (6), 143-145

The composition diagram for up to 33 at.% Ba-Pd alloys was constructed and showed that $BaPd_5$ and $BaPd_2$ are present.

Energy Bands in β' -PdIn

S. J. CHO, *Phys. Status Solidi*, 1970, **41**, (1), 179-189

The energy bands for ordered β' -PdIn were calculated by the augmented plane wave method. The possible open orbits were studied, and the electronic density of states curve was obtained from the energy bands. Estimates of the electronic specific heat coefficient, the magnetic susceptibility, and the cyclotron effective masses are given. Results are compared with existing optical data.

Remarkable Interstitial Hydrogen Contents Observed in Rhodium-Palladium Alloys at High Pressures

T. B. FLANAGAN, B. BARANOWSKII and S. MAJCHRZAK, *J. Phys. Chem.*, 1970, **74**, (24), 4299-4300

A H:Pd atomic ratio greater than 1 was found in an alloy system, Rh-Pd, where the added metal is probably a nonabsorber of H_2 . At 2300-5100 atm stoichiometric 1:1 hydrides were obtained for the 20% and 30% Rh-Pd alloys. Either Rh can absorb H_2 but at a higher pressure than Pd, or Rh functions as a H_2 absorber only when in the Pd matrix.

The Thermodynamic Properties of Solid Palladium-rich Pd-Cd, Pd-In, Pd-Sn and Pd-Sb Alloys

J. B. DARBY, K. M. MYLES and J. N. PRATT, *Acta Metall.*, 1971, **19**, (1), 7-14

Vapour pressure measurements were used to calculate the activities and free energies of formation, at 1350 K, of Pd-rich Pd-Co alloys. Entropy of formation values were found by combining free energy results with heats of formation (ΔH_f) at 298 K. ΔH_f values were also found at 298 K for the α -phase Pd-rich alloys of the polyvalent solutes In, Sn, Sb and for the intermediate phases PdSb and PdSb₂. Results suggest some correlation between the four alloy systems.

Thermoelectric Power of Palladium Based Dilute Alloys

D. GAINON and J. SIERRO, *Helv. Phys. Acta*, 1970, **43**, (6-7), 541-554

The thermopower, S , of 1 at.% M-Pd (where M = Ti, V, Cr, Mn, Fe, Co, Ru, Re, Os, Te) was measured at 1.5-273 K. For the ferromagnetic alloys a change of slope of S exists near the Curie temperature. Pd-Cr shows a large positive

value of S at low temperature, but for the other alloys S is both positive and greater than when the same dilute elements are dissolved in noble metals, but is not anomalously dependent on temperature.

Composition Diagram of the Ti-Ir System

V. N. EREMENKO and T. D. SHTEPA, *Izv. Akad. Nauk S.S.S.R., Metall.*, 1970, (6), 197-203

Studies of the Ti-Ir system indicated a stable CsCl-type phase in 30-40 at.% Ir-Ti at high temperatures based on Ti-Ir stabilised with extra Ti. No eutectoid decomposing to β -phase at 500°C was found.

Photoelectric Determination of the Work Function of Ru Films as a Function of Sintering Temperature (78K-925K)

R. BOUWMAN and W. H. M. SACTLER, *Surface Sci.*, 1971, 24, (1), 140-148

The photoelectric work function ϕ of a Ru film on a Pyrex substrate rises from 4.52 ± 0.03 eV at 78K to 5.02 ± 0.03 eV at 573K after sintering. For Ru on quartz and annealed above 700K, $\phi = 5.10 \pm 0.05$ eV. The emission constant continues to decrease even beyond the temperature where ϕ ceases to increase. Theoretical values of ϕ for Rh and Os are given as 5.1-5.2 and 4.9-5.0 respectively.

Physico-chemical Behaviour of Ruthenium in Sea Water

P. GUEGUENIAT, *Comm. Energie Atom. Bull. Inform. Sci. Tech.*, 1970, (151), 27-32

Results are presented of a physico-chemical study of nitrosylruthenium compounds discharged into the sea by spent fuel processing plants. Various forms of these derivatives are separated on an ion exchange resin, and their concentration is correlated with time and with certain properties of the water.

Optical Properties of Molybdenum and Ruthenium

K. A. KRESS and G. J. LAPEYRE, *J. Opt. Soc. Am.*, 1970, 60, (12), 1681-1684

Reflectance values for Ru were obtained at 0.5-14 eV. The graph of the imaginary part of the dielectric constant ϵ_2 against $h\nu$ has a shoulder at 1.6 eV, and the loss functions $\text{Im}[1/\epsilon]$ and $\text{Im}[1/(1+\epsilon)]$ shows peaks at 10.2 and 8.7 eV respectively.

Electron Work Function in Alloys of Tantalum with Ruthenium

O. K. KULTASHEV and A. P. MAKAROV, *Fiz. Metal. Metalloved.*, 1970, 30, (5), 924-928

Thermoelectronic emission studies showed a sharp rise in the electron work function of >5% solutions of Ru and Ta, explained by the formation of monoatomic films of Ru on the surface of the solid solution, and a work function

for solid solutions of Ta in Ru near to that of pure Ru, 4.75 eV. The μ phase has the largest electron work function in the system, 5.05 eV.

CHEMICAL COMPOUNDS

Nuclear Magnetic Resonance in PtSb₂ and PtAs₂

G. R. MALLICK and P. R. EMTAGE, *Phys. Rev. B*, 1970, 2, (5), 1251-1260

Analysis of n.m.r. results for Sb¹²¹, Sb¹²³, and Pt¹⁹⁵ in PtSb₂ and PtAs₂, and of the observed anisotropy in the Pt resonance suggest that Pt is in the formal valency state (-2), and that all bonds in these compounds are primarily covalent.

Free Enthalpy of Formation of Palladium Oxide

H. KLEYKAMP, *Z. Phys. Chem.*, 1970, 71, (1-3), 142-148

The free enthalpy of formation of PdO was obtained using a solid cell Pt/Fe₃FeO/ZrO₂.Y₂O₃/Pd,PdO/Pt. The standard entropy of PdO was calculated using the specific heat and entropies of Pd and O₂ as 8.8 ± 0.5 cal/g/mol. Using this and the free enthalpy functions of Pd, O₂ and PdO, the value of -28,200 ± 500 cal/mol was got for free enthalpy of formation of PdO.

Metal-Boron Compounds. X. Diborylamines as π -Ligands in Palladium Complexes

G. SCHMID and L. WEBER, *Z. Naturf. B*, 1970, 25, (10), 1083-1086

Bis(dimethylamino)boronchloride reacts with (C₆H₅CN)₂PdCl to form complexes of the type Cl₂Pd[(CH₃)₂N]₂BX (X = Cl, CH₃). The analogous bromo- and iodoboranes react with coordinated benzonitrile to form C₆H₅C(X₂)N-B(N[(CH₃)₂])₂PdX (X = Br, I) which are probably dimeric. The B-N groups act as π ligands.

Synthesis and Structure of a New High-pressure Form of Rh₂O₃

R. D. SHANNON and C. T. PREWITT, *J. Solid State Chem.*, 1970, 2, (1), 134-136

A new high pressure form of Rh₂O₃ was prepared at 64 kbar and 1200°C. The material is a semiconductor with a resistivity of 130 Ω cm at room temperature and an activation energy of 0.16 eV. The structure is orthorhombic with $a = 5.1686$, $b = 5.3814$, $c = 7.2426$ Å, $Z = 4$, $D_{\text{obs}} = 8.28$ g/cm³, and is described as containing layers of a corundum-like structure cut parallel to (10 $\bar{1}$ 1) and then stacked together.

Starting Materials for the Preparation of Organometallic Complexes of Platinum and Palladium

F. R. HARTLEY, *Organomet. Chem. Rev. A, Subj. Rev.*, 1970, 6, (1), 119-137

The preparation of zerovalent and divalent com-

plexes of Pt and Pd with PPh_3 and divalent benzonitrile, ethylene and amine complexes with Pd and Pt are described.

The Chemistry of Transition Metal Carbonyls. Synthesis and Reactivity

E. W. ABEL and F. G. A. STONE, *Q. Rev.*, 1970, **24**, (4), 498-552

The preparation and properties of many transition metal carbonyls including those of the platinum group metals are described.

ELECTROCHEMISTRY

Electrocatalytic Activity of Platinum-Ruthenium Alloy Black for Methanol Oxidation

M. WATANABE, T. SUZUKI and S. MOTOO, *Denki Kagaku*, 1970, **38**, (12), 927-932

The dependence of the activity on the composition of Pt-Ru alloys was investigated. Pt and Ru were alloyed with Ti and developed in HF solutions to give the black, which is a f.c.c. solid solution of Ru in Pt. The catalytic activity increased sharply till the Ru:Pt ratio was 2, then decreased sharply till the ratio was 3. It is proposed that the Pt atom requires 2-3 Ru atoms as its nearest neighbours for maximum electrocatalytic activity.

Anion Adsorption on Palladium

V. S. VILINSKAYA, R. H. BURSHEIN and M. R. TARASEVICH, *Elektrokhimiya*, 1970, **6**, (10), 1497-1502

Bond strength and H_2 chemisorption on Pd decrease and anion adsorption increases when Pd powder is observed in the series of acids H_2SO_4 , H_3PO_4 , HCl, HBr.

Mechanism of the Chlorine Electrode Reaction on Platinum, Iridium and Rhodium in Aqueous Hydrochloric Acid

T. YOKOYAMA and M. ENYO, *Electrochim. Acta*, 1970, **15**, (12), 1921-1943

The mechanism of the reaction $2\text{Cl}^- \rightleftharpoons \text{Cl}_2 + 2e^-$ was studied on smooth Pt, Ir and Rh in aqueous HCl. For Pt and Ir the reaction occurs in two distinct steps; which of these is the rate determining step depends on the electrode potential. For Rh the results are incomplete.

ELECTRODEPOSITION AND SURFACE COATINGS

Precious Metal Plating

P. G. L. VIVIAN, *Electroplating Met. Finish.*, 1970, **23**, (11), 20-22, 24, 26, 28

A review of electroplating techniques for Pd and Rh is given. The type of deposit, different methods, and the problems involved are discussed. Pt and Ru are briefly mentioned. A short account of electroless plating is also given.

The Nucleation and Growth of Electroless Metal Deposited on Plastic Substrates

A. RANTELL, *Trans. Inst. Metal Finish.*, 1970, **48**, (5), 191-198

A technique is described for obtaining electron micrographs of very thin electroless metal films deposited on plastic substrates. During the early stages of growth, electroless metals are deposited as island structures, growth beginning at active sites created by the $\text{SnCl}_2/\text{PdCl}_2$ treatment. These active Pd sites are less numerous on surfaces where the depositing metal is chemically bonded to the plastic than when it is not.

Electroplating of Osmium

A. J. APPLEBY, *J. Electrochem. Soc.*, 1970, **117**, (12), 1610

Attempts were made to form an Os electrode using a Au cathode, and a graphite anode in a molten electrolyte of 8% OsCl_3 in KCN-NaCN. At 10-20 mA/cm² a bright, adherent though granular deposit was obtained. At higher current densities black deposits occurred. Typical roughness factors for bright deposits were 6-7.

HETEROGENEOUS CATALYSIS

Reaction between Deuterium and Cyclic Olefins on Platinum/Alumina in the Liquid Phase

J. J. PHILLIPSON and R. L. BURWELL, *J. Am. Chem. Soc.*, 1970, **92**, (21), 6125-6133

The liquid phase reactions between D_2 and cyclopentene, cyclohexene, cycloheptene, cyclooctene, bicyclo(3,3,0)-2-octene and 1-hexene on Pt/ Al_2O_3 were studied in various solvents. The exchange reaction proceeds rapidly, the D^*/H^* ratio increasing over the low value obtained with no solvent or in THF. The distribution of products and effect of solvents are discussed.

Poisoning Studies in a Single-pellet Catalytic Reactor

J. L. HAHN and E. E. PETERSON, *Canad. J. Chem. Engng.*, 1970, **48**, (2), 147-150

The activity of a 0.25% Pt/ η - Al_2O_3 catalyst was measured using the cyclopropane hydrogenolysis reaction. The catalyst was progressively poisoned from the outside to the centre plane non-uniformly. Results suggest a bi-modal pore size distribution in the pellet.

Mathematical Description of Platforming Carried out in Severe Conditions

YU. M. KHOROV, G. M. PANCHENKOV and I. YA. SHAPIRO, *Khim. Tekhnol., Topliv Masel*, 1970, (11), 37-40

A mathematical model of the reactions occurring during petroleum reforming over Pt catalysts is based on the conversions between gas, paraffins, naphthalenes, and aromatic hydrocarbons.

Structure of Platinum/Alumina Catalysts for Gasoline Reforming

M. MOSER, L. VAJTA and I. SZEKENYI, *Kem. Kozlem.*, 1970, **33**, (3), 255-263

Electron microscopy showed the distribution of Pt in Pt/Al₂O₃ catalysts. Micrographs are given of Sinclair Baker 0.35% Pt/Al₂O₃ and Soviet AP-56 0.55-0.60% Pt/Al₂O₃.

The Role of C₅- and C₆-Dehydrocyclisation in the Aromatisation of *n*-Octane on Platinum/Alumina Catalyst

V. G. VLASOV, YU. V. FOMICHEV and B. A. KAZANSKII, *Neftekhimiya*, 1970, **10**, (6), 821-825

Studies of the conversion of *n*-octane and *n*-propylcyclopentane on Pt/Al₂O₃ with added alkali, (0.6% Pt + 0.8% Na₂O₃)/ γ -Al₂O₃, showed that aromatisation of *n*-octane is accompanied by C₅-dehydrocyclisation to form alkylcyclopentanes in both acidic and alkaline catalysts and that, on acidic catalyst, alkylcyclopentanes play a significant part in aromatics formation. Decreasing the acidity of Pt/Al₂O₃ by Na₂O addition causes unsaturated hydrocarbons to appear in the conversion products.

Isomerisation and Dehydrocyclisation of Hexanes over Monofunctional Supported Platinum Catalysts

F. M. DAUTZENBERG and J. C. PLATTEUW, *J. Catalysis*, 1970, **19**, (1), 41-48

Isomerisation and dehydrocyclisation reactions of hexanes in the presence of Pt/Al₂O₃ catalysts were studied. The dehydrocyclisation of *n*-hexane to C₆H₆ goes by two different routes; by a Pt-catalysed six ring closure, or, by a thermal six ring closure of hexatrienes by dehydrogenation of *n*-hexane over Pt.

Electron Microscope Investigation of Platinum Catalysts. I. Platinum on Aluminium Oxide

L. M. KEFFELI, *Zh. Fiz. Khim.*, 1970, **44**, (11), 2820-2823

The formation of Pt crystals on Al₂O₃ by the thermal decomposition of H₂PtCl₆ comprises the formation of a crystal lattice from Pt atoms, its coarsening, growth of these first crystals on single centres, their agglomeration, and the role of the carrier in the process.

Rheniforming Scores High in Commercial Runs

G. D. GOULD and C. S. MCCOY, *Oil Gas J.*, 1970, **68**, (48, Nov. 30), 49-53

The performance of Re-Pt catalysts for petroleum reforming is reviewed. They are found to maintain selectivity, to give stable yields and can be regenerated. They have a lower fouling rate and greater stability than Pt/Al₂O₃ catalysts. They operate efficiently at reduced pressures, which increases the yield and quality of the product.

Mixed Adsorption Catalysts. V. Catalysis of Hydrogen Peroxide by Platinum-Silver Systems on Diamagnetic Charcoal from Sugar

I. A. ZUBOVICH, *Zh. Fiz. Khim.*, 1970, **44**, (10), 2536-2540

Studies of the activity of Pt-Ag catalysts supported on batches of decalcified diamagnetic sugar charcoal in the reaction of H₂O₂ at 23, 35 and 55°C showed that reductions in activity are caused by formation of mPt.nAg complexes on the surface, where m and n are the simplest stoichiometric ratio. Apparent activation energies and the pre-exponential multiple in the Arrhenius equation are directly related but the activity of the catalysts is inversely related to them.

Contrast between Nickel and Platinum Catalysts in Hydrogenolysis of Saturated Hydrocarbons

H. MATSUMOTO, Y. SAITO and Y. YONEDA, *J. Catalysis*, 1970, **19**, (2), 101-112

The mechanisms of hydrogenolysis on Ni/SiO₂ and Pt/SiO₂ are compared. The reaction on Pt occurs via heterolytic splitting of the C-H bond on adsorption. On Ni the splitting is homolytic. This is due to the greater stability of Pt-H coordination over Ni-H coordination.

Adsorption of Benzene and Cyclohexane on Zeolite Y Supported Platinum Catalyst

M. KOBAYASHI and T. SHIRASAKI, *Kogyo Kagaku Zasshi*, 1970, **73**, (6), 1245-1247

The adsorption of C₆H₆ and cyclohexane on Pt/Zeolite Y catalysts containing water was studied. The water did not desorb on adsorption of cyclohexane, but did with C₆H₆. On changing the carrier gas from N₂ to H₂ adsorbed C₆H₆ was converted to cyclohexane which was desorbed. The results indicate three types of catalyst site; a vacant site, sites with adsorbed water and having Pt particles, and sites with adsorbed water but no Pt particles.

Effect of the Nature and the Amount of Secondary Components of Binary Palladium Alloys on their Catalytic Activity in Relation to the Dehydrogenation of Cyclohexane

V. M. GRYAZNOV, V. P. POLYAKOVA, E. M. SAVITSKII, L. FRADES, E. V. KHIRAPOVA, E. KHURES and G. V. SHKOLA, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1970, (11), 2520-2524

Studies on the catalytic dehydrogenation of cyclohexane showed that activity increased with Pt content up to 1.5% Pt-Pd but that it decreased with Ag content in the range 20 up to 50% Ag-Pd. 5% Ni-Pd is more active but 10% Ni-Pd is less active than Pd. Apart from Pt-Pd alloys, the apparent activation energies of these alloys in this reaction are similar to that of Pd. The activity of B-Pd alloys is not large and is unstable.

Relation between Drift Potential of Catalyst and Reaction Rate in Liquid-phase Hydrogenation Processes. VII. Investigation of the Catalytic Properties of Raney Nickel Promoted by Palladium

V. A. DRUZ', T. D. GLADYSHEVA and D. V. SOKOL'SKII, *Kinet. Kataliz.*, 1970, **11**, (5), 1274-1278

The introduction of Pd to Raney Ni catalysts does not change the effectiveness of the catalyst surface but greatly increases its useful area, apparently because Pd increases the amount of dissolved H₂ and its diffusion rate. The greater number of active centres may be due to the formation of Ni-Pd centres.

Adsorption and Catalytic Properties of Palladium-Iridium Electrode Catalysts

A. A. SUTYAGINA, L. G. KOPEVA and G. P. KHOMCHENKO, *Vest. Moskov. Univ., Ser. II, Khim.*, 1970, **25**, (5), 562-567

A study of the adsorptive and catalytic properties of electrodeposited Pd, Ir, and Pd-Ir alloys showed that H₂ adsorption decreases with increasing Ir content and that catalytic activity relates to alloy composition; e.g. the catalytic activity of >15% Ir-Pd in hydrogenation and CH₃NO₂ electroreduction in 0.1 N H₂SO₄ was greater than that of pure Pd or Ir.

Adsorption of Hydrogen on Hydrogenation Catalysts in Solution. V. Adsorption and Heat of Adsorption of Hydrogen on Os and Ru Blacks in 0.1 N H₂SO₄ Solutions

YU. A. PODVYAZIN and G. P. GRECHUSHKINA, *Zh. Fiz. Khim.*, 1970, **44**, (10), 2529-2531

Charging curves were used to study the adsorption of H₂ on Os and Ru blacks in 0.1 N H₂SO₄ at 0-50°C, and the differential heat of adsorption of H₂ was calculated. It decreased linearly from 12.5-1.7 kcal/mole as H₂ coverage of Os black rose from 0.1 to 0.9. Results for Ru were similar.

Hydrogenation of Dimethylethynylcarbinol on Ruthenium-Palladium Supported Catalysts in Various Solvents

D. V. SOKOL'SKII, T. M. DUKHOVNAYA and K. K. DZHARDAMALIEVA, *Ibid.*, (11), 2833-2836

The maximum activity of Ru-Pd/Al₂O₃ catalysts for hydrogenation of dimethylethynylcarbinols occurs with 20.8 at.% Ru-Pd and is unrelated to the solvent in tests with H₂O, C₂H₅OH and aqueous and alcoholic KOH solutions. The solvents do not affect the kinetics of the process. Changing the reaction temperature does not alter the general form of the relation.

Effect of the Structure on the Dehydrogenation Rate of Secondary Alcohols on Platinum, Palladium and Rhodium Catalysts

M. HAJEK, J. C. DUCHET and K. KOCHLOEFL, *Coll. Czech. Chem. Commun.*, 1970, **35**, (8) 2258-2274

The kinetics of dehydrogenation were studied

for aliphatic secondary alcohols at 200°C on Pt, Pd and Rh on kieselguhr. The initial rate of dehydrogenation depends on the alcohol partial pressure. On Pt the initial reaction rate and adsorption coefficient are influenced by steric effects of the substituents; on Rh or Pd polar effects have more significance.

HOMOGENEOUS CATALYSIS

The Palladium Chloride Catalysed Cyclodimerisation of 1-Methylcyclopropene

F. J. WEIGERT, R. L. BAIRD and J. R. SHAPLEY, *J. Am. Chem. Soc.*, 1970, **92**, (22), 6630-6635

1-Methylcyclopropene undergoes a thermal oligomerisation in the presence or absence of free-radical inhibitors. With the Pd catalyst a facile cyclodimerisation predominates.

Specificity of the Kinetics of Oxidation of Ethylene to Acetaldehyde in the Presence of Complexes of Palladium with 1,2-Naphthoquinone-4-sulphoxide

N. B. SHITOVA, K. I. MATVEEV and G. I. ELIZAROVA, *Kinet. Kataliz.*, 1970, **11**, (5), 1152-1158

The mechanism of Pd in the oxidation of C₂H₄ to CH₃CHO with complex catalysts of Pd with 1,2-naphthoquinone-4-sulphoxide (NQS) was explained by comparing the regularity of the reaction kinetics with results based on the stages of oxidation of Pd in the process and on the formation of the complex of Pd(II) with NQS.

Organic Synthesis by Means of Noble Metal Compounds. XLII. Reaction of Butadiene and Aldehydes Catalysed by Palladium Triphenylphosphine Complexes

K. OHNO, T. MITSUYASU and J. TSUJI, *Tetrahedron Letters*, 1971, (1), 67-70

Butadiene reacted with aldehydes such as benzaldehyde to give products such as 1-phenyl-2-vinyl-4,6-heptadien-1-ol and 2-phenyl-3,6-divinyltetrahydropyran. The relative amounts of the two products was controlled by the molar ratio PPh₃/Pd in the catalyst. A mechanism is discussed.

The Hydroformylation of Nitroalkenes with Rhodium Carbonyl

M. TAKESADA and W. WAKAMATSU, *Bull. Chem. Soc. Japan*, 1970, **43**, (7), 2191-2194

Nitrobenzene was hydrogenated to aniline using [Rh(CO)₃]₄ above 150°C. Other nitroalkenes were also converted to their corresponding aldehydes; good yields were obtained at 60-70°C.

Hydroformylation of Olefins in the Presence of Ru₃(CO)₁₂

G. BRACA, G. SBRANA, F. PIACENTI and P. PINO, *Chim. e Ind.*, 1970, **52**, (11), 1091-1096

The hydroformylation occurred in more drastic

conditions than with Co catalysts. The isomeric distribution of products is not altered by the conditions in the area studied. The influence of the concentrations of the reactants and catalyst was investigated for cyclohexene.

Decarbonylation of Allylic Alcohols Using Rhodium(I) Complexes

A. EMBERY, A. C. OEHLSLAGER and A. M. UNRAU, *Tetrahedron Letters*, 1970, (50), 4401-4403

Decarbonylation of allylic alcohols, e.g. converting *cis*-but-2-ene-1,4-diol to 1-propanol was carried out using $(\text{Ph}_3\text{P})_3\text{RhCl}$ at 110-150°C in aceto- and benzonitrile.

A Study of the Hydrogenation of Cycloalkenes with Homogeneous Rhodium Complexes as Catalysts

Y. TAKEUCHI, *Diss. Abstr. B*, 1970, 30, (10), 4572-4573

The use of $(\text{Ph}_3\text{P})_3\text{RhCl}$ as a homogeneous catalyst in the hydrogenation of cycloalkenes in a benzene or benzene-ethanol solution is reported. Effects of using different solvents and varying the ligands of the Rh(I) complex are discussed.

Speed of Homogeneous Catalytic Hydrogenation of Unsaturated Compounds with $\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$

W. STROHMEIER and R. ENDRES, *Z. Naturf. B*, 1970, 25, (9), 1068-1069

The rate of hydrogenation depends on the nature of the unsaturated compound. Olefins and esters react more quickly if they contain terminal double bonds. For olefins the rates are; 1-olefins > 2-*cis*- > 2-*trans*- > 3-*trans*-olefins; also, alkenes > alkynes. Substitution of a H atom by halogen decreases the reactivity.

The Reactivity of the Hydrogenation Catalysts $\text{MeH}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_3$ (Me = Rh, Ir) on Unsaturated Compounds

W. STROHMEIER and S. HOFMANN, *Ibid.*, (11), 1309-1310

The Rh complex was more active and selective than the Ir one in all cases. This behaviour, and the difference in adduct formation and dissociation in benzene between the two complexes is discussed in the light of increased electron density of the Ir atom over the Rh.

Further Observations on the Catalytic Transformation of Benzoic Anhydrides into Fluorenones and Biphenyls

J. BLUM, D. MILSTEIN and Y. SASSON, *J. Org. Chem.*, 1970, 35, (10), 3233-3237

A study of the catalytic conversion of benzoic anhydrides into fluorenones and biphenyls by several Rh complexes indicated that mixtures of aromatic anhydrides react generally as if they were mixed anhydrides, leading to the formation of asymmetrically substituted products.

Homogeneous Hydroformylation of Alkenes with Hydridocarbonyltris(triphenylphosphine)rhodium(I) as Catalyst

C. K. BROWN and G. WILKINSON, *J. Chem. Soc., A, Inorg. Phys. Theor.*, 1970, (17), 2753-2764

$\text{RhH}(\text{CO})(\text{PPh}_3)_3$ is an excellent catalyst for hydroformylation of alkenes at 25°C at 1 atm. From alk-1-enes high ratios of straight chain to branched chain aldehydes can be produced. The dependence of rates and products on catalyst and substrate concentrations and partial pressures of H_2 and CO, temperature and added excess of PPh_3 are described.

The Protonation of Ruthenium- and Rhodium-bridged Carboxylates and Their Use as Homogeneous Hydrogenation Catalysts for Unsaturated Substances

P. LEGZDINS, R. W. MITCHELL, G. L. REMPEL, J. D. RUDDICK and G. WILKINSON, *J. Chem. Soc., A, Inorg. Phys. Theor.*, 1970, (19), 3322-3326

The protonation of rhodium(II) acetate by non-complexing, non-oxidising acids such as HBF_4 gives the green Rh^{4+} . The interaction with PPh_3 and CO gives complexes $\text{Rh}(\text{PPh}_3)_3\text{BF}_4$ and $\text{Rh}(\text{CO})(\text{PPh}_3)_3\text{BF}_4$. The acetate $\text{Ru}_2(\text{OCOMe})_4$ and its adducts with PPh_3 and pyridine were characterised. Methanolic HBF_4 solutions of Rh(II) and Ru(II) acetates and of $\text{Ru}_2(\text{OAc})_4\text{Cl}$ in the presence of PPh_3 are active catalysts for the homogeneous hydrogenation of alkenes, alkynes and other unsaturated substances.

Homogeneous Polymerisation of Butadiene Catalysed by Ruthenium Complex-Tertiary Phosphine System

K. HIRAKI and H. HIRAI, *Macromolecules*, 1970, 3, (4), 382-387

Butadiene was polymerised using dichloro(dodeca-2,6,10-triene-1,12-diyl)ruthenium(IV)- or dichloro- μ -chlorobis(2,7-dimethylocta-2,6-diene-1,8-diyl)diruthenium(IV)tertiaryphosphine catalyst. The polybutadiene had *cis*-1,4-, *trans*-1,4- and *trans*-1,2-unit contents of 37-60, 20-32 and 13-34%; the molecular weight was $2.6-4.8 \times 10^3$. The n.m.r. spectra of the catalysts was investigated.

CHEMICAL TECHNOLOGY

Anodic Discharge of Chloride Ions on Pt-Ir Alloy Electrodes

G. FAITA, G. FIORI and A. NIDOLA, *J. Electrochem. Soc.*, 1970, 117, (10), 1333-1335

The behaviour of Ti-supported Pt-Ir alloys in the electrolysis of NaCl was examined as a function of Ir content, NaCl concentration and electrolysis time. An Ir content as low as 0.5% was sufficient to eliminate the passivation effects. Not less than 5-10% Ir is necessary to have low potentials after thousands of hours.

ELECTRICAL AND ELECTRONIC ENGINEERING

Semiconductors Produced by Doping Oxide-glasses with Ir, Pd, Rh or Ru

C. C. SARTAIN, W. D. RYDEN and A. W. LAWSON, *J. Non-crystalline Solids*, 1970, **4**, 231

Semiconductors were produced by diffusion doping oxide glasses with more than 1 wt.% of Ir, Pd, or Ru and by implanting 40 keV Ir ions into several oxide glasses. The properties and methods of conduction in the semiconductors is discussed.

TEMPERATURE MEASUREMENT

New Reference Tables for Platinum 10% Rhodium/Platinum and Platinum 13% Rhodium/Platinum Thermocouples - An Interim Report

R. E. BEDFORD, *I.S.A. Trans.*, 1970, **9**, (3), 248-253
Existing reference tables for Pt:10%Rh-Pt and Pt:13%Rh-Pt thermocouples are known to be partially inaccurate and are being revised jointly by the NBS, NPL and NRC (Canada). Details are given of the progress to date and some of the results are presented and discussed.

Selection of Thermocouples for Temperature Profiling of Semiconductor Diffusion Furnaces

I. O. NIELSON, *Solid State Technol.*, 1970, **13**, (10), 33-38, 55

Pt:13%Rh-Pt thermocouples are discussed in terms of their best characteristics for temperature profiling. The criteria for selection, care of the thermocouples, evaluation of the materials and the calibration are all discussed.

Noncatalytic Coating for Platinum-Rhodium Thermocouples

J. H. KENT, *Combust. Flame*, 1970, **14**, (2), 279-281
A mixture of Y oxide and Be oxide (10-15%) gave a good noncatalytic coating for Pt-Rh thermocouples. A series of thin coats of a solution of 6-8% Be oxide in a solution of YCl in HCl was applied to give a coating ≈ 0.015 mm on 0.12 mm wire, after firing at 1600°C.

Measurement of Temperature in Corrosive Melts

V. E. PERFILOVA, S. V. BODYACHEVSKII, L. A. AVVAKUMOVA and A. S. DERMAN, *Izv. Akad. Nauk S.S.S.R., Ser. Fiz.*, 1970, **34**, (6), 1203-1205

A Pt-clad Rh-Pt thermocouple is superior to refractory-clad Rh-Pt thermocouples at 900-1400°C in BaO-B₂O₃ and PbO-PbF₂-B₂O₃ melts.

NEW PATENTS

METALS AND ALLOYS

Gold-based Spinnerette Alloy

JOHNSON, MATTHEY & CO. LTD.
U.S. Patent 3,529,959

A gold-based spinnerette alloy contains between 50% and 80% Au, between 0.04 and 0.5% Ir and the remaining part Pt, apart from the impurities. A method of making the alloy consists of induction melting the components, casting a sheet and homogenising.

CHEMICAL COMPOUNDS

Osmium Carbonyl

JOHNSON, MATTHEY & CO. LTD.
U.S. Patent 3,508,870

Method of preparing Os carbonyls is described. A solution of OsO₄ in an inert hydrocarbon solvent is heated to an elevated temperature under super-atmospheric pressure in the presence of CO. The product is primarily Os₃(CO)₁₂ with traces of Os₄O₄(CO)₁₂.

ELECTRODEPOSITION AND SURFACE COATINGS

Coating or Inlaying

JOHNSON, MATTHEY & CO. LTD.
British Patent 1,207,970

A Cu or Cu alloy is coated or inlaid with a thin layer of a noble metal such as Au, Ag, Pd or Pt or alloys thereof by interposing between the two a layer of Ni, Fe, Co, Mo, or V, and heating the three layers under pressure to bond them.

Reductive Vapour Deposition of Osmium

ENGLISH ELECTRIC VALVE CO. LTD.
British Patent 1,209,318

High purity Os deposits are obtained on a surface by vapour deposition from an OsO₄/H₂ mixture. OsO₄ is dissolved in water at room temperature and H₂ (or a gas containing H₂) bubbled through the solution. The resulting gas is mixed with another reducing gas to give a predetermined ratio of OsO₄ to reducing gas. In contact with a hot body this gas deposits metallic Os.