

# ABSTRACTS

of current literature on the platinum metals and their alloys

## PROPERTIES

### Absolute Seebeck Coefficient of Platinum from 80 to 340K and the Thermal and Electrical Conductivities of Lead from 80 to 400K

J. P. MOORE and R. S. GRAVES, *J. Appl. Phys.*, 1973, **44**, (3), 1174-1178

The absolute Seebeck coefficient of Pt was determined at 80-340K by direct comparison to Pb. Results are compared with previous data and observed differences are discussed.

### The Adsorption and Decomposition of CO on Pt(III)

J. M. MARTINEZ and J. B. HUDSON, *J. Vacuum Sci. Technol.*, 1973, **10**, (1), 35-38

A cylindrical mirror electron energy analyser was used to study adsorption of CO on Pt(III). Agreement of the results with those obtained by the flash filament technique allowed absolute calibration of the Auger spectrometry system used to measure surface C and O concentrations. Beam-induced decomposition of adsorbed CO at high fluxes contaminated the surface with C. CO adsorption rate and saturation coverage decreased with increasing contamination. Adsorption rate approached zero at high C concentrations.

### Determination of Anisotropy Constants and Saturation Magnetisation and Magnetic Properties of Powders of Iron-Platinum Alloys

O. A. IVANOV, L. V. SOLINA, V. A. DEMSHINA and L. M. MAGAT, *Fiz. Metal. Metalloved.*, 1973, **35**, (1), 92-97

Equiatomic FePt alloy at 20°C has anisotropy constant  $K_1 = 7 \times 10^7$  erg/cm<sup>3</sup> and saturation magnetisation  $I_s = 1150$  gauss. Magnetic properties of FePt powder depend on the effective grain size rather than the actual grain size. Alloys have high  $H_c$  related to their crystallite domain structure and high anisotropy.

### The Vanadium-Platinum Constitution Diagram

R. M. WATERSTRAT, *Metall. Trans.*, 1973, **4**, (2), 455-466

The phase diagram for the V-Pt system was established over the entire composition range using metallography, X-ray diffraction and electron microprobe techniques. Four equilibrium intermediate phases were identified and characterised crystallographically; they are stable

to progressively higher temperatures with increasing V content. Ribbons of the VPt phase (orthorhombic, AuCd type structure), strongly coherent with the face-centred cubic phase matrix, were observed in ~43 at.% V-Pt alloys, suggesting the possibility of fibre reinforcement.

### Order-hardening of CuPt

R. S. IRANI and R. W. CAHN, *Acta Metall.*, 1973, **21**, (5), 575-584

The microhardness of equiatomic and Pt-rich Cu-Pt alloys was measured after isothermal annealing at various temperatures below  $T_c$ . The hardness passed through a maximum which varied with temperature and was highest for CuPt for a given temperature. Below 620°C, coarse ordered domains, only slightly harder than the disordered alloy, formed near the grain boundaries. This suggests that hardness is determined by domain size as well as by lattice misfit strains.

### The Constitution and Structure of Some Rare Earth-Platinum Alloys in the Range 20-35% Rare Earth

I. R. HARRIS, W. E. GARDNER and R. H. TAYLOR, *J. Less-common Metals*, 1973, **31**, (1), 151-158

Lattice parameter measurements on rare earth-Pt alloys showed that the  $C_{15}$ -type structure is stable in the range 24.2-31.8 at.% Gd-Pt and that  $GdPt_2$  lies in a two-phase region. Arc-melted  $TbPt_3$  has the  $C_{15}$ -type structure but is converted to  $L_{12}$ -type by annealing at 1173K. At low temperatures, the two types have very different magnetic susceptibilities.

### The Magnetic Properties of Alloys of Palladium and Gadolinium, Dysprosium and Holmium

O. LOEBICH and E. RAUB, *J. Less-common Metals*, 1973, **31**, (1), 111-118

The magnetic susceptibilities of 0-100 at.% Pd-rare earth alloys were measured at 140-720K. The results suggest that Gd, Dy and Ho ions are always trivalent. In the solid-solution range, the 4d shell of Pd is filled as rare earth concentration increases.

### Effect of Pressure on the Low-temperature Electrical Resistance of Pure Pd and Very Dilute Pd:Ni Alloys

R. A. BEYERLEIN and D. LAZARUS, *Phys. Rev. B*, 1973, **7**, (1), 511-524

The electrical resistivity of pure Pd and 0.32, 0.55 and 1.0 at.% Ni-Pd was measured at low temper-

atures under He pressure  $\sim 4.5$  kbar. Results are compared to those for a localised-exchange-enhancement model. Results for 1.0% Ni-Pd indicate that the formula for temperature-dependent resistivity for  $T < 10\text{K}$ ,  $\rho = \rho_0 + AT^2 + BT^5$ , is inadequate. A large reversible decrease in residual resistivity of each alloy occurred on application of pressure. A model is proposed for the role of Ni in this effect.

#### Effect of Phosphorus Concentration on the Atomic Distribution Function of Amorphous Pd-Ni-P Alloys

J. DIXMIER and P. DUWEZ, *J. Appl. Phys.*, 1973, **44**, (3), 1189-1193

The effect of phosphorus concentration on the atomic distribution function in amorphous alloys  $(\text{Pd}_{50}\text{-Ni}_{50})_{100-x}\text{P}_x$ , where  $x = 15-27.5$ , was studied. The intensity of the first peak of the interference function decreases with increasing P-content while the second peak has a definite shoulder on the right side for alloys low in P which disappears as the P-concentration increases.

#### Role of Chemical Bonding in Metallic Glasses

H. S. CHEN and B. K. PARK, *Acta Metall.*, 1973, **21**, (4), 395-400

The effects of composition on the densities and stabilities of glassy Pd-Cu-Si alloys were studied. Properties of these alloys are apparently dominated by chemical bonding rather than relative atomic sizes.

#### Investigation of the Solubility of Hydrogen in Palladium-Silver Alloys

V. A. PUGACHEV, E. I. NIKOLAEV, F. I. BUSOL, B. P. NAM and I. N. SHABALIN, *Zh. Fiz.Khim.*, 1973, **47**, (1), 36-40

Studies on 10, 20, 23, 26, 29, and 40% Ag-Pd alloys at 100-500°C showed that at 300-500°C the greatest  $\text{H}_2$  solubility occurs with 40% Ag-Pd, whereas at lower temperatures it occurs for progressively lower Ag contents, and at 100°C in pure Pd. At 300-500°C solubility is given by  $S = S_0 \exp(\Delta H/RT)$ .  $S_0$  and  $\Delta H$  were calculated from experimental data and the shape of the curve  $S = f(1/T)$  is interpreted as due to two solid solutions of  $\text{H}_2$  in Pd and Ag-Pd alloys.

#### A High-pressure Investigation of the Rhodium/Palladium/Hydrogen System

B. BARANOWSKI, S. MAJCHRZAK and T. B. FLANAGAN, *J. Phys. Chem.*, 1973, **77**, (1), 35-39

The absorption of  $\text{H}_2$  at high pressure by 0-80 at.% Rh-Pd alloys was investigated by electrical resistivity measurements. The alloys absorbed large quantities of  $\text{H}_2$ : e.g. at 5100 atm, 25°C, atomic ratio values of H:Pd = 1.44 and H:metal = 1.00 were obtained, showing that Rh absorbs H in a Pd matrix. Conditions necessary for hydride formation are discussed.

#### The Crystal Structure of $\text{V}_3\text{Rh}_5$

R. M. WATERSTRAT and B. DICKENS, *J. Less-common Metals*, 1973, **31**, (1), 61-67

The crystal structure of  $\text{V}_3\text{Rh}_5$  was investigated by X-ray diffraction and classified as a new type containing both ordered and disordered sites in a pseudo-hexagonal unit cell. The structure is intermediate between the  $\text{Cu}_3\text{Au}$  and  $\text{CuAu}$  types of ordering but has a two-layer stacking sequence instead of three.

#### The Solubility of Hydrogen in Rhodium, Ruthenium, Iridium and Nickel

R. B. McLELLAN and W. A. OATES, *Acta Metall.*, 1973, **21**, (3), 181-185

The temperature variation of solubility of H in Rh, Ru, Ir and Ni was measured by equilibrating the samples with ultrapure  $\text{H}_2$  at 1 atm then quenching and analysing them. The solubilities are all small (0.005-0.05 at.% H) and are consistent with the quasi-regular model for dilute interstitial solid solutions. The relative partial enthalpy and excess entropy of the dissolved H atoms were calculated.

#### Adsorption of Carbon Monoxide on Ruthenium

S. CHARKABORTTY and H. E. GRENGA, *J. Appl. Phys.*, 1973, **44**, (1), 500-501

The adsorption and desorption of CO on  $(10\bar{1}1)$ ,  $(10\bar{1}0)$ ,  $(11\bar{2}2)$  and  $(20\bar{2}1)$  regions of Ru was studied. Both physisorbed CO and  $\beta$ -CO were found on all regions, while  $\alpha$ -CO was found only on low-index  $(10\bar{1}1)$  and  $(10\bar{1}0)$  regions. Substrate and/or adsorbate rearrangements also occur on all regions.

#### Mechanical Properties and Structures of the Heat-treated Zr-Ru and Zr-Pd Alloys

H. KIMURA and S. UEHARA, *J. Japan Inst. Metals*, 1973, **37**, (2), 247-251

Strength and hardness of Zr-Ru and Zr-Pd increased with increasing Ru or Pd content up to  $\sim 1$  or 0.5 at.% respectively.  $< 1$  at.% Ru or Pd, ductility of Zr was not affected and elongation at break was  $> 30\%$ . Alloys quenched from  $> 655^\circ\text{C}$  (Ru) or  $755^\circ\text{C}$  (Pd) were harder than annealed alloys. Age-hardening occurred in the quenched alloys, particularly in 1 at.% Ru-Zr. The martensitic structure of the quenched alloys is shown in transmission electron micrographs.

#### Mass-spectrometric Study of the Ruthenium-Carbon System

B. M. MOLLAKOV, M. P. GLAZUNOV and V. I. SPITSYN, *Izv. Akad. Nauk S.S.S.R., Ser.Khim.*, 1973, (3), 660-661

Ru carbide exists at 2000-2250K and the dissociation energy of the molecules is  $149 \pm 5$  kcal/M. The heats of sublimation of Ru and Ru carbide from the Ru-C system are  $155 \pm 2$  and  $175 \pm 2$  kcal/M respectively.

## CHEMICAL COMPOUNDS

### The Enhanced Therapeutic Effect of *cis*-Platinum(II) Diamminodichloride against L1210 Leukemia When Combined with Cyclophosphamide or 1,2-Bis(3,5-dioxopiperazine-1-yl) propane or Several Other Antitumour Agents

R. J. WOODMAN, A. E. SIRICA, M. GANG, I. KLINE and J. M. VENDITTI, *Chemotherapy*, 1973, 18, (3), 169-183

In mice with early leukemia L1210, combinations of *cis*-Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> with cyclophosphamide, isophosphamide, 1,2-bis(3,5-dioxopiperazine-1-yl) propane (ICRF-159), or emetine at least doubled the increase in lifespan achieved with individual drugs. *Cis*-Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> was also more effective against advanced leukemia when combined with cyclophosphamide or ICRF-159.

### Binding of *cis*- and *trans*-Dichlorodiammineplatinum(II) to Nucleosides. I. Location of the Binding Sites

S. MANSY, B. ROSENBERG and A. J. THOMSON, *J. Am. Chem. Soc.*, 1973, 95, (5), 1633-1640

The interaction of *cis*- and *trans*-Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> with nucleic acid components was studied by u.v. spectrometry at 37°C. Bidentate binding was distinguished from monodentate. The location of the sites of attack on the nucleosides was discussed.

### Magnetic Susceptibility $\chi$ of K<sub>2</sub>Pt(CN)<sub>4</sub> Br<sub>0.3</sub> · 2.3(H<sub>2</sub>O)

A. MENTH and M. J. RICE, *Helv. Phys. Acta*, 1972, 45, (6), 900

Low temperature measurements of  $\chi$  show a temperature dependent diamagnetic susceptibility, which can be separated into a dominant temperature independent diamagnetism  $\chi_d$  and a temperature dependent paramagnetism  $\chi_p$ . Results are discussed in terms of a model of linear metallic strands interrupted by insulating lattice defects and of a one-dimensional Hubbard model.

### Electronic Absorption Spectra of Platinum(II) Centres in Liquid Alkali Metal Chlorides

G. N. PAPATHEODOROU and G. P. SMITH, *J. Inorg. Nucl. Chem.*, 1973, 35, (3), 799-807

The optical electronic absorption spectra of Pt(II) centres were measured in liquid CsCl, KCl, LiCl and CsCl-LiCl and KCl-LiCl mixtures. In CsCl at 650-700°C and the eutectic mixtures below ~400°C the spectrum is that expected for normal square-planar PtCl<sub>4</sub><sup>2-</sup> complex anions at elevated temperatures. In LiCl and the mixed solvents at elevated temperatures the spectrum is modified by a drawing together of the two spin-allowed bands. This effect is attributed to the polarisation of PtCl<sub>4</sub><sup>2-</sup> by the outer shell of Li<sup>+</sup> ions.

## Dinitrogen Complexes of the Transition Metals

A. D. ALLEN, R. O. HARRIS, B. R. LOESCHER, J. R. STEVENS and R. N. WHITELEY, *Chem. Rev.*, 1973, 73, (1), 11-20

Dinitrogen complexes of transition metals, including Pt, Ir, Os, Rh and Ru, may be prepared by direct use of N<sub>2</sub>, by combination of 2N atoms or from compounds containing chains of N atoms. The chemical, magnetic, structural and bonding properties of these complexes are reviewed.

### Cationic Cyclic Carbene or Carbon-bonded Ylide Complexes of Iridium(III) and Platinum(II)

P. J. FRAZER, W. R. ROPER and F. G. A. STONE, *J. Organometal. Chem.*, 1973, 50, (1), C54-C56

2-Chloro-4-methylthiazole, 2-chlorobenzoxazole and 2-chlorobenzthiazole oxidatively add to both IrCl(CO)(PMe<sub>2</sub>Ph)<sub>2</sub> and Pt(PhCH=CHPh)(PEt<sub>3</sub>)<sub>2</sub>. Protonation of the products at nitrogen produces cationic carbene complexes.

### The Crystal Structure of Tetracaesium- $\mu$ -oxo-decachlorodiosmate(IV), Cs<sub>4</sub>[Os<sub>2</sub>OCl<sub>10</sub>]

K. F. TEBBE and H. G. VON SCHNERING, *Z. Anorg. Allgem. Chem.*, 1973, 396, (1), 66-80

The anhydrous binuclear complex Cs<sub>4</sub>[Os<sub>2</sub>OCl<sub>10</sub>] crystallises with an orthorhombic unit cell, Pcab, with a=12.521Å, b=13.994Å, c=11.798Å and Z=4. The complex anion forms corner-sharing octahedra tetragonally deformed. Interatomic distances are given, and the crystal structure is compared with that of analogous complexes.

### Oxidative Addition Reactions of Triphenylphosphine with Dodecacarbonyltriosmium

C. W. BRADFORD and R. S. NYHOLM, *J. Chem. Soc., Dalton Trans.*, 1973, (5), 529-533

Os<sub>3</sub>(CO)<sub>12</sub> and PPh<sub>3</sub> reacted together in a molar ratio of 1:2 to give a mixture of the mono-, di- and tri-substituted derivatives. Six other compounds also occurred in the mixture including unusual new ones: HOs<sub>3</sub>(CO)<sub>8</sub> and Os<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>(PPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), HOs<sub>3</sub>(CO)<sub>7</sub>(PPh<sub>2</sub>)(PPh<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>), Os<sub>3</sub>(CO)<sub>8</sub>(PPh<sub>2</sub>)(Ph)(PPhC<sub>6</sub>H<sub>4</sub>) and Os<sub>3</sub>(CO)<sub>7</sub>(PPh<sub>2</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>). The properties, structures and i.r., n.m.r. and mass spectra of the compounds were determined.

## ELECTROCHEMISTRY

### The Influence of Halide Ions on Methanol Adsorption and Oxidation on a Platinised Electrode

J. SOBKOŃSKI and A. WIECKOWSKI, *J. Electroanal. Chem. Interfac. Electrochem.*, 1973, 41, (3), 373-379

The kinetics of MeOH chemisorption on a platinised electrode at +0.5V were studied. The

adsorption rate decreases in the presence of halide ions during simultaneous adsorption and, when halide ions are added to the solution, previously adsorbed MeOH is completely removed from the surface only in the case of Cl ions. Adsorbed intermediates react with Br and I ions and the reaction products remain strongly bound to the surface, being only partially oxidised at +1.2V.

### The Behaviour of Platinum, Iridium and Ruthenium Electrodes in Strong Chloride Solutions

A. T. KUHN and P. M. WRIGHT, *J. Electroanal. Chem. Interfac. Electrochem.*, 1973, **41**, (3), 329-349.

The behaviour of Pt, Ir and Ru electrodes was studied in 0.5 M H<sub>2</sub>SO<sub>4</sub>, 2M NaCl+10<sup>-2</sup>M HCl and in 5M NaCl+10<sup>-2</sup>M HCl. Pt is strongly influenced by the specific adsorption of Cl<sup>-</sup> ions, while Ir shows evidence of oxide formation in H<sub>2</sub>SO<sub>4</sub> but does not show any dependence on Cl<sup>-</sup> ion adsorption. Ru electrodes corrode relatively easily, which in strong chloride solution causes a modification in the properties of the electrode.

### The Kinetics of Chlorine Evolution and Reduction on Titanium-supported Metal Oxides Especially RuO<sub>2</sub> and IrO<sub>2</sub>

A. T. KUHN and C. J. MORTIMER, *J. Electrochem. Soc.*, 1973, **120**, (2), 231-236

I/V curves were determined for RuO<sub>2</sub>- and IrO<sub>2</sub>-coated Ti electrodes under conditions typically encountered in the chlor-alkali industry. Definite electrocatalytic effects were found although, in general, linear Tafel behaviour was not observed.

## ELECTRODEPOSITION AND SURFACE COATINGS

### A New Protective Coating for Nickel Alloys

G. LEHNERT and H. W. MEINHARDT, *Electrodep. Surf. Treatment*, 1973, **1**, (3), 189-197

Increased turbine inlet temperatures in aircraft engines necessitate the use of internal cooling channels resulting in thinner blade walls. The coatings on the Ni superalloy blades therefore must have greater high temperature corrosion and oxidation resistance and thermal shock resistance, even as thin coatings; they must be able to protect the inner surfaces and must not reduce the mechanical strength of thin blades. These requirements are fulfilled by LDC-2—a duplex coating of electroplated Pt followed by aluminising; Pt prevents continued diffusion of Al.

### Fundamentals of Ion Plating

D. M. MATTOX, *J. Vacuum Sci. Technol.*, 1973, **10**, (1), 47-52

Ion plating processes involve the subjection of the substrate to a flux of high energy ions which cause

sputter cleaning before and during film formation. Ion plating is used in adhesion, corrosion protection and electrical contact applications. It can provide a clean substrate surface, a high surface temperature without bulk heating, physical mixing of film and substrate material, and an influence on nucleation and growth of the film. The techniques are described with examples including a Pd/stainless steel catalyst and PtSi/Si.

## HETEROGENEOUS CATALYSIS

### Investigation of the Efficiency of Pt-Zeolite Catalysts in the Decomposition of H<sub>2</sub>O<sub>2</sub>

#### III. Activity of Pt-Zeolite Catalysts, Produced by Impregnation on CaY Zeolite

T. G. MARTYNYUK, T. A. POSPELOVA, V. I. SHEKHOBALOVA and N. I. KOBOZEV, *Zh. Fiz. Khim.*, 1973, **47**, (2), 406-409

Pt/CaY zeolite (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=4.8) catalysts were prepared by impregnation of H<sub>2</sub>PtCl<sub>6</sub> solution. Their activity and efficiency for H<sub>2</sub>O<sub>2</sub> decomposition are greatest when the Pt concentration is 3-4 wt.% and differ from results with NaY zeolite. Activation energies of catalysts in 0.2-16N H<sub>2</sub>O<sub>2</sub> solutions change inversely with activity. Activation energies of 4% Pt catalysts are 9 and 13 kcal/mole for CaY and NaY zeolites respectively. Differences may be caused by the different surface structures which affect the active Pt centres and their activity.

### Determination and Effect of Platinum Concentration Profiles in Supported Catalysts

J. F. ROTH and T. E. REICHARD, *J. Res. Inst. Catalysis, Hokkaido Univ.*, 1972, **20**, (2), 85-94

Radial concentration profiles of Pt on cylindrical Al<sub>2</sub>O<sub>3</sub> pellets were determined by electron-probe microanalysis. Very low Pt concentrations can be measured quantitatively and profiles can be determined for catalysts containing both uniform and non-uniform Pt distributions. Dehydrogenation results indicated that catalytic activity is higher with uniform Pt distribution.

### Microfocused X-ray Diffraction Examination of Pt/Al<sub>2</sub>O<sub>3</sub> Catalysts before and after Engine Dynamometer Ageing

K. MIYAZAKI, *J. Catalysis*, 1973, **28**, (2), 245-253

Two types of commercial 0.5 % Pt/Al<sub>2</sub>O<sub>3</sub> catalyst pellets were observed during ageing in non-leaded exhaust gas using a microfocused X-ray diffraction technique. The dispersed Pt-Al<sub>2</sub>O<sub>3</sub> layer, extending 100-200 μm from the surface, possessed a disordered crystalline arrangement different from the usual form of Pt and from the matrix. The Pt which was initially more highly crystalline had a higher activity for CO and hydrocarbon oxidation than the amorphous Pt catalyst. Deactivation was closely associated with alteration in surface layer crystalline orientation.

### On the Role of Vinylnaphthalene in the Dehydrocyclisation of 1-Ethyl-naphthalene in the Presence of Platinum/Alumina Catalysts

L. A. ERIVANSKAYA, A. KHALIMA-MANSUR and A. F. PLATE, *Neftekhimiya*, 1973, **13**, (1), 27-31

Dehydrocyclisation over 0.5 wt.% Pt/Al<sub>2</sub>O<sub>3</sub> of ethyl-naphthalene in He includes the intermediate formation of vinylnaphthalene but in H<sub>2</sub> there is direct conversion to acenaphthene. The yield of dehydrocyclisation products in H<sub>2</sub> is greater than in He.

### Dehydrogenation and Hydrogenolysis of Acenaphthene in the Presence of Platinum/Alumina Catalysts

A. KHALIMA-MANSUR, L. A. ERIVANSKAYA and A. F. PLATE, *Neftekhimiya*, 1973, **13**, (1), 32-35

Dehydrogenation and hydrogenolysis of acenaphthene over 0.5 wt.% Pt/Al<sub>2</sub>O<sub>3</sub> at 370-500°C showed that the main product of hydrogenolysis is 1-ethyl-naphthalene. Experiment at 460°C and calculations for 370-627°C gave the equilibrium composition of the acenaphthylene-acenaphthene mixture.

### Effect of Palladium on the Activity of Platinum/Alumina Catalysts in the Aromatisation of Hydrocarbons

V. N. SELEZNEV, YU. V. FOMICHEV and M. E. LEVINTER, *Neftekhimiya*, 1973, **13**, (1), 36-40

Tests on the activity of Pt/Al<sub>2</sub>O<sub>3</sub> to which Pd had been added showed that, in aromatisations of *n*-hexane, *n*-heptane and methylcyclopentane, the catalyst with 0.3 wt.% each of Pt and Pd has no more activity for dehydrocyclisation of *n*-hexane and *n*-heptane than has 0.6 wt.% Pt/Al<sub>2</sub>O<sub>3</sub> but that the activity for dehydroisomerisation of methylcyclopentane is rather greater.

### Hydrogenation of Ethylene on Zeolites Containing Group VIII Metals

KH. M. MINACHEV, V. I. GARANIN and T. A. NOVUZOV, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1973, (2), 330-333

The activities of faujasite, synthetic mordenite and amorphous aluminosilicates containing Pt, Pd and Ni for hydrogenation of C<sub>2</sub>H<sub>4</sub> depend on the natures of the support and the metal and on the method of deposition of the metal on the support. Orders of activity are Pt/NaY ~ Pt/NaX > PtAl<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub> > Pt/NaM and Pt/NaY > Pd/NaY ≫ Ni/NaY. Treatment of Pt/NaY by air and by reduction with H<sub>2</sub> above 400°C causes reduced activity for hydrogenation.

### Catalytic Hydrogenation of Benzene and Nitrobenzene on Platinum-Rhodium Alloys

T. M. GRISHINA and G. D. VOVCHEV, *Zh. Fiz. Khim.*, 1973, **47**, (2), 413-415

Catalytic hydrogenations of C<sub>6</sub>H<sub>6</sub> and C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> on Pt, Rh and Rh-Pt alloys were used to establish

the state of those alloys with maximum activity, which is probably due to the greater absorption of H<sub>2</sub> by the alloys and their lower bonding energy.

### Isocyanate Intermediates in Ammonia Formation over Noble Catalysts for Automobile Exhaust Reactions

M. L. UNLAND, *Science*, 1973, **179**, (4073), 567-569

Isocyanate species were detected on the surface of Pt metal catalysts on Al<sub>2</sub>O<sub>3</sub> during reactions of CO with NO. I.r. spectral intensity for surface isocyanate agrees with the tendency to form NH<sub>3</sub> on noble metals. The isocyanate species suggests a new route to NH<sub>3</sub> formed during catalytic reduction of NO<sub>x</sub> in automobile exhausts.

### Sulphides of the Platinum Metals as Catalysts for the Reduction of Nitro Compounds

V. F. SVIDCHENKO, YU. T. NIKOLAEV and D. V. SOKOL'SKII, *Zh. Fiz. Khim.*, 1973, **47**, (3), 725-727

Reductions of C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> and *m*-nitrobenzenesulphoxide over Ru, Rh, Pt and Pd sulphides showed that Rh sulphide is most active for reduction of C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>; for nitrobenzenesulphoxide, Pt sulphide was most active in aqueous solutions, and Rh sulphide was most active in aqueous-alcoholic solutions.

### Effect of the Structure of Olefins on the Transfer of Multiple Bonds in the Presence of Ruthenium, Rhodium and Palladium

I. V. GOSTUNSKAYA, N. B. DOBROSERDOVA, A. I. TRINKO and B. A. KAZANSKII, *Neftekhimiya*, 1973, **13**, (1), 17-20

Studies of double bond transfer in  $\alpha$ -olefins during liquid phase hydrogenation over Pd, Ru and Rh blacks showed that transfer occurs more in the presence of Pd and Rh but less on Ru when there are methyl radicals at the second C atom of the olefin. This is due to the difference in sign of the charge of active H on these metals.

### Hydrogenation of Dimethylethynylcarbinol on Colloidal Palladium Catalyst Stabilised by Polyvinyl Alcohol

O. A. TYURENKOVA, V. A. DASHEVSKII and N. G. USHIVETS, *Zh. Fiz. Khim.*, 1973, **47**, (1), 74-77

Potentiometry was used to study hydrogenation of dimethylethynylcarbinol on 5% Pd colloidal catalyst stabilised by polyvinyl alcohol.

### The Structure and Catalytic Properties of Palladium-Silver and Palladium-Gold Alloys

E. G. ALLISON and G. C. BOND, *Catal. Rev.*, 1972, **7**, (2), 233-289

The general physical properties and catalytic properties of a range of Pd-Au alloys are reviewed. The preparation of both supported and unsupported catalysts is described, and a number of chemisorption and catalytic reactions are discussed.

## The Structure and Activity of Supported Metal Catalysts. VII. CO Poisoning and Metal Location in Palladium-Charcoal Catalysts

D. POPE, D. S. WALKER and R. L. MOSS, *J. Catalysis*, 1973, **28**, (1), 46-53

It was observed that the life of a Pd/C catalyst for  $C_2H_4$  hydrogenation in the presence of traces of CO is dependent on the location of the Pd crystallites within the charcoal granules, as shown in electron micrographs. This was confirmed by correlation between diffusion-limited hydrogenation rates in liquid-phase reactions and CO poisoning times for  $C_2H_4$  hydrogenation. These times could form a basis for characterisation of such catalysts with respect to metal location.

## Catalytic Reduction of Nitrobenzene on Mixed Palladium-Rhodium Catalysts on Alumina Substrates

D. V. SOKOL'SKII, N. M. POPOVA and L. A. SOKOLOVA, *Izv. Akad. Nauk Kaz. S.S.R., Ser. Khim.*, 1972, **22**, (5), 10-15

The most active Pd-Rh catalyst investigated for reduction of  $PhNO_2$  to  $PhNH_2$  in EtOH was prepared by precipitating the metal hydroxides on to  $Al_2O_3$  from an aqueous solution of  $PdCl_2$  and  $\leq 0.4$  equiv  $RhCl_3$  using  $Na_2CO_3$  solution, and then reducing with  $H_2$  at  $350^\circ C$ . At higher Rh contents, rate decreased and activation energy increased.

## Hydrogenation of Cyclohexene on Ruthenium-Palladium Supported Catalysts

D. V. SOKOL'SKII, T. M. DUKHOVNAYA and K. K. DZHARDAMALIEVA, *Izv. Akad. Nauk Kaz. S.S.R., Ser. Khim.*, 1972, **22**, (5), 16-20

A wide range of Ru-Pd catalysts was investigated for the hydrogenation of cyclohexene and  $HOCMe_2C:CH$  in EtOH; the most active was 5%, 10.5 at.% Ru-Pd/ $Al_2O_3$ . A  $BaSO_4$  support decreased the rate because of adsorption of the products. Hydrogenation of cyclohexene is a mixed-order reaction, the rate-determining step being its adsorption on the catalyst.

## The Chemisorption of CO on Ruthenium Metals and Ruthenium-Silica Catalysts

M. KOBAYASHI and T. SHIRASAKI, *J. Catalysis*, 1973, **28**, (2), 289-295

The chemisorption of CO on Ru/ $SiO_2$  catalysts and on Ru metal powders prepared by Adams's method and by Willstätter's method (reduction of  $H_2PtCl_6$  using HCHO solution) was measured by static and pulse methods at  $150^\circ C$ . Adams Ru adsorbed a normal amount of CO but Willstätter Ru and Ru/ $SiO_2$  adsorbed a large volume of CO which decreased on repetition of adsorption and reduction. In fresh Ru/ $SiO_2$  samples  $CO:Ru > 1$  and suggested the presence of  $Ru-(CO)_2$ ,  $Ru-(CO)_3$ , etc., species in the chemisorption, confirmed by  $Ru_3(CO)_{12}$  bands in the i.r. spectra.

## HOMOGENEOUS CATALYSIS

### Hydrogenation of Organic Compounds Using Homogeneous Catalysts

R. E. HARMON, S. K. GUPTA and D. J. BROWN, *Chem. Rev.*, 1973, **73**, (1), 21-52

An extensive review is presented of the scope, mechanisms and variable factors of homogeneous catalysts for organic compound hydrogenation. A wide range of homogeneous catalysts, many of them based on Pt group metals, has been developed in recent years. Because of the high stereoselectivity of these catalysts, it is possible to design a system for almost every hydrogenation.

### Catalytic Carboxylation of Fats. Carboxy Acids and Esters from Mono-unsaturates

E. M. FRANKEL and F. L. THOMAS, *J. Am. Oil Chem. Soc.*, 1973, **50**, (2), 39-43

Pt group metals catalysts were investigated for the one-step selective hydrocarboxylation of oleic acid to carboxystearic acid. A mixture of  $PdCl_2$  and  $PPh_3$  was very effective and was more active than performed  $(PPh_3)_2PdCl_2$ . Pd/C with  $PPh_3$  and HCl was also a good catalyst system. At  $120-150^\circ C$ , 3000-4000 lb/in<sup>2</sup> CO pressure, with or without AcO solvents, yields were 85-99%. The C-9 and C-10 isomers, in approximately equal proportions, were 87-94% of the yield.

### Palladium-catalysed Syntheses of Aromatic Coupling Compounds

H. IATAAKI and H. YOSHIMOTO, *J. Org. Chem.*, 1973, **38**, (1), 76-79

The oxidative coupling of aromatic compounds under  $O_2$  pressure in the presence of Pd acetate was investigated. Acac and EDTA greatly increased the yield of coupling products but acids, bases, LiCl, polar solvents and some metal ions inhibited the reaction. The method could be used to prepare biphenyltetracarboxylic acids from *o*-xylene, dimethyl phthalate and naphthalene.

### Hydrogenation and Isomerisation of Allyl Alcohol and Cyclohexenol-3 in the Presence of Chlorodimethylsulphoxide Complexes of Palladium and Rhodium

L. KH. FREIDLIN, YU. A. KOPYTSEV and N. M. NAZAROVA, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1973, (3), 700-701

Chlorodimethylsulphoxide complexes of Pd catalyse hydrogenation of  $C=C$  bonds in allyl alcohol and cyclohexenol-3, and also their conversion to propionaldehyde and cyclohexanol, respectively. The complexes of Rh promote hydrogenation of allyl alcohol, both in the presence and absence of  $H_2$ , and the reduction of propionaldehyde, but are poisoned by acrolein. Pd complexes, however, accelerate hydrogenation of acrolein but are inert with respect to propionaldehyde.

## Mechanism of the Homogeneous Hydrogenation of Olefins Catalysed by Chlorocarbonyltris (triphenylphosphine) iridium (I) with and without Basic Cocatalysts

M. G. BURNETT, R. J. MORRISON and C. J. STRUGNELL, *J. Chem. Soc., Dalton Trans.*, 1973, (7), 701-708

In a polar solvent, the rate of hydrogenation of olefins catalysed by  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  increased to a maximum during an induction period. In toluene, or when a radical inhibitor was added, the induction period did not occur. The delay was attributed to radical side chain reactions. Basic cocatalysts in polar solvents converted the catalyst to  $\text{IrH}_3(\text{CO})(\text{PPh}_3)_2$ . The hydrogenation mechanism is discussed in terms of an Ir-olefin intermediate.

## Selective Hydrogenation of 1,5,9-Cyclododecatriene to Cyclododecene Catalysed by Ruthenium Complexes

D. R. FAHEY, *J. Org. Chem.*, 1973, 38, (1), 80-87

The selective homogeneous hydrogenation of 1,5,9-cyclododecatriene (CDT) to cyclododecene—important in the synthesis of polyamide monomers—is catalysed by Ru complexes, especially  $(\text{PPh}_3)_2(\text{CO})_2\text{RuCl}_2$  which gives yields of 98.5% at 125-160°C, 100-200 lb/in<sup>2</sup> H<sub>2</sub>; it can be formed directly from RuCl<sub>3</sub>, PPh<sub>3</sub> and CO in situ. At least 32,100 mol of CDT can be selectively hydrogenated per mole of  $(\text{PPh}_3)_2(\text{CO})_2\text{RuCl}_2$ . Rate measurements suggest the hydrogenation is first order in olefin and catalyst.

# NEW PATENTS

## METALS AND ALLOYS

### Cladding Alloys

LEACH & GARDNER CO. *British Patent* 1,310,082  
Cladding alloys, especially for a core of Be-Cu, contain 40-60 wt. % Au, 9.6-14.4% Pd, 4.8-7.2% Ag and Ni, 19.2-28.8% Cu and 1.6-2.4% Zn. They replace more expensive Au, Ag and Pt alloys, e.g. in spring contacts.

### Palladium Alloy-Silver Alloy Composite Materials

MATSUSHITA ELECTRIC INDUSTRIAL CO. LTD.  
*British Patent* 1,312,151

A composite material intended for electrical contacts consists of a Pd alloy sheet and an Ag alloy sheet bonded together using a Ni-Cu sheet at 720-850°C and rolled to required thickness.

### Graphite/Noble Metal Mixtures

BRITISH PETROLEUM CO. LTD.  
*British Patent* 1,312,273

A mixture of graphite and Pt, Au or Ag is obtained

## CHEMICAL TECHNOLOGY

### The Preparation and Purification of Americium Metal by Evaporation

J. C. SPIRLET and W. MÜLLER, *J. Less-common Metals*, 1973, 31, (1), 35-46

In order to redetermine its physical and chemical properties several grams of <sup>241</sup>Am were prepared by thermal dissociation of Pt<sub>5</sub>Am, formed by the reduction of AmO<sub>3</sub> with ultrapure H<sub>2</sub> in the presence of Pt powder. The Am metal was purified by sublimation at 1100°C, 10<sup>-6</sup> Torr. Metal impurities were analysed by emission spectrography, and O, N and H by vacuum hot extraction. Amounts of O, N and H were ≤250, 50 and 20 p.p.m. respectively.

## TEMPERATURE MEASUREMENT

### Temperature Control Using a Platinum Resistance Sensor

G. D. BRABSON and A. A. FANNIN, *Rev. Sci. Instrum.*, 1973, 44, (3), 338

Improved control of a constant temperature bath is achieved using a Pt resistance thermometer in a resistance bridge to generate an error signal proportional to the difference between actual and desired temperatures. The error signal, ~0.4mV/°C, is ten times the magnitude of the Chromel-Alumel thermocouple signal it replaces.

by grinding a natural or synthetic graphite with Pt, Au or Ag in an organic liquid to give a surface area of at least 5 m<sup>2</sup>/g. This mixture can be used in lubricants.

### Platinum Metal Alloys

JOHNSON MATTHEY & CO. LTD.  
*U.S. Patent* 3,709,667

Dispersion-strengthened Pt group metals and alloys are produced by introducing an oxide refractory precursor such as Zr as an alloying additive. The alloy formed is converted to powder, cold worked, oxidised to give an oxide in the powder and then compacted and sintered.

### Sprayed Metal Articles

JOHNSON MATTHEY & CO. LTD.  
*Dutch Appl.* 71.11161

Metal articles are produced by arc, flame or plasma spraying Pt or Pt alloy droplets at a cold target to form a coherent layer of individual particles which are then mechanically worked to a mass.