

# ABSTRACTS

of current literature on the platinum metals and their alloys

## PROPERTIES

### The Mechanism of Crystallographic Ordering in CuPt

R. S. IRANI and R. W. CAHN, *J. Mater. Sci.*, 1973, 8, (10), 1453-1472

Studies of the ordering of the Cu-Pt system near to the Cu-Pt composition showed that Pt-rich off-stoichiometric alloys contain a wide two-phase region of order and disordered platelets. Two types of diffraction sequence were observed in isothermally ordered stoichiometric alloys. Those annealed at  $620^{\circ}\text{C} < T < 815^{\circ}\text{C}$  showed a series of broad, asymmetric X-ray line profiles during the early part of the ordering cycle, representing a "continuous" reaction but those annealed below  $620^{\circ}\text{C}$  showed evidence of co-existence of both ordered and disordered phases, representing a "discontinuous" reaction. A nucleation-and-growth model is proposed for CuPt at all ordering temperatures. Microscopic studies indicated a lamellar structure above  $620^{\circ}\text{C}$  but a grain-boundary reaction, generating very coarse domains, below it. Samples annealed below  $475^{\circ}\text{C}$  had ordered spherulites grow within the grains. Samples cooled slowly through  $T_c = 815^{\circ}\text{C}$  order by a diffusion-controlled shear process.

### Investigations on the Systems of Platinum and of Rhenium with Mercury

G. JANGG and T. DÖRTBUDAK, *Z. Metallkunde*, 1973, 64, (10), 715-719

Partial pressure studies on Pt amalgams confirmed the existence of  $\text{PtHg}_{43}$ ,  $\text{PtHg}_2$  and  $\text{PtHg}$ .  $\text{PtHg}_1$  and  $\text{PtHg}_2$  are stable at  $200-500^{\circ}\text{C}$ .  $\text{PtHg}$  decomposes eutectoidally at  $250^{\circ}\text{C}$  into  $\text{PtHg}_2$  and Hg-saturated Pt. All three phases have at most very narrow regions of homogeneity. Their thermodynamic data could be derived from vapour pressure measurements. Solubility studies showed that Os, Ir, Ru, and Re, which form no compounds with Hg, are only very slightly soluble in it; Rh is slightly more soluble in it ( $6 \times 10^{-5}$  wt.% at  $500^{\circ}\text{C}$ ) and does form compounds with Hg; Pt and Pd form compounds with Hg and their solubilities in it at  $300^{\circ}\text{C}$  are  $8 \times 10^{-4}$  and 0.2 wt.% respectively.

### Crystal Growth and Characterisation of $\text{PtP}_2$

A. BAGHDADI, A. FINLEY, P. RUSSO, R. J. ARNOTT, and A. WOLD, *J. Less-common Metals*, 1974, 34, (1), 31-38

$\text{PtP}_2$  crystals grown from a Sn flux were shown to be of good quality by magnetic, density and crystallographic measurements. The crystals

were diamagnetic, with susceptibility  $-64 \times 10^{-6}$  e.m.u./mole and P—P bond distance 2.22Å.

### Pressure against Composition Isotherms and Thermodynamic Data for the $\alpha$ -Phase of the Palladium/Hydrogen System

R. BURCH and N. B. FRANCIS, *J. Chem. Soc., Faraday Trans. 1*, 1973, 69, (11), 1978-1982

Pressure/composition isotherms were determined for the  $\alpha$ -phase of the Pd/H system at  $372-724\text{K}$  by direct equilibration with gaseous  $\text{H}_2$ . The partial molar enthalpy and partial molar entropy of solution of H in Pd were derived as a function of composition, the values at  $600\text{K}$  being respectively  $-15.56\text{kJ/mol. H}_2$  and  $-96.5\text{J}^{\circ}\text{K/mol.H}_2$ .

### Diffusion of Hydrogen in Rhodium-Palladium Alloys

D. ARTMAN and T. B. FLANAGAN, *J. Phys. Chem.*, 1973, 73, (23), 2804-2807

Diffusion constants were determined for interstitial  $\text{H}_2$  in a series of random f.c.c. Rh-Pd alloys and the diffusion parameters were determined at small  $\text{H}_2$  contents.

### Diffusion Investigations in the System Palladium-Titanium by Means of Electron Probe Micronanalysis

P. LAMPARTER, T. KRABICHLER and S. STEEB, *Z. Metallkunde*, 1973, 64, (10), 720-724

Electron probe studies of diffusion processes at  $600-1000^{\circ}\text{C}$  in the Pd-Ti system showed  $d(\text{Ti})$  and  $\beta(\text{Ti})$  solid solubility and the phases  $\text{TiPd}$ ,  $\text{TiPd}_2$ ,  $\text{Ti}_2\text{Pd}_3$ , and  $\text{TiPd}_3$ . Thickness  $d$  of single phases grows as  $d \sim \sqrt{t}$ . Interdiffusion coefficients were obtained by Matano's method and their temperature dependence led to determination of their activation energy.

### Comprehensive Plastic Deformation of a Bulk Metallic Glass

C. A. PAMPILLO and H. S. CHEN, *Mater. Sci. Engng.*, 1974, 13, (2), 181-188

Compressive plastic deformation experiments at  $77-520\text{K}$  were made on a bulk  $\text{Pd}_{0.775}\text{Cu}_{0.06}\text{Si}_{0.165}$  glass. At  $100-500\text{K}$  the ratio of the stress to the elastic modulus is  $\sim 1/60$ , independent of temperature.

### Physicochemical Properties of Metallic Melts Based on Palladium

N. A. VATOLIN and E. L. DUBININ, *Fiz.-Khim. Osn. Met. Protsessov*, 1973, 266-278

Activities, heats of mixing, vapour pressures,

viscosities, electrical resistances, magnetic susceptibilities, density, and surface tensions were determined and discussed for the Pd-Ni, Pd-Co, Pd-Cu, Pd-Ag, Pd-Fe, Pd-Cr, Pd-Mn, Pd-Sb, Pd-Pb, Pd-Al, Pd-Si, and Pd-W systems.

### The Crystal Structure and Lattice Constants of $RE_3Pd_4$ , $Y_3Pd_4$ and $Th_3Pd_4$ Compounds

A. PALENZONA and A. IANDELLI, *J. Less-common Metals*, 1974, **34**, (1), 121-124

Alloys of the rare earths, Y, Th, Hf, and U with Pd of the  $M_3Pd_4$  composition were studied. With the exception of Eu, V and Hf, single phases were formed, crystallising with  $Pu_3Pd_4$ -type structure. The stability was restricted for radius ratio ( $R_m/R_{Pd}$ ) to 1.20 and 1.37.

### Upper Critical Fields and Critical Currents of Superconducting Zirconium-Rhodium Alloys

K. TOGANO and K. TACHIGAWA, *J. Less-common Metals*, 1973, **33**, (2), 275-282

Trigonal  $Zr_2Rh$  has a high superconducting transition temperature but contains no Group Va element. Studies of 3, 14 and 33 at. % Rh-Zr alloys showed that 33 at. % Rh-Zr consists of  $Zr_2Rh$  columnar crystals with [001] simple fibre texture and substructures. The superconducting critical field  $H_{c2}$  of  $Zr_2Rh$  is as high as 80 kOe at 4.2K, despite its relatively low normal state resistivity, and has crystallographic anisotropy, i.e.  $H_{c2}$  is higher perpendicular to the columnar axis. Critical current density  $J_c$  of 14 and 33 at. % Rh-Zr is related to the metallographic structures.

### Reflectance and Optical Constants of Evaporated Ruthenium in the Vacuum Ultraviolet from 300 to 2,000Å

J. T. COX, G. HASS, J. B. RAMSAY and W. R. HUNTER, *J. Opt. Soc. Am.*, 1973, **63**, (10), 1281, abstr.

Studies of Ru films at 300-2000Å showed that variation of deposition from 1 to 80Å/s by electron bombardment on the glass and quartz substrates had little effect on their reflectance. Reflectance loss during extended exposure to air was small, i.e. oxide film formation is low. Films made on substrates at 300°C had slightly higher reflectance than those made at 40°C. Interference effects made 150-200Å semitransparent films have higher reflectance than opaque films ~584Å thick. Near 2000Å films 300Å thick had highest reflectance. Ru films under optimum conditions had 26% reflectance at  $\lambda=584\text{Å}$ .

### Effect of Zirconium on Conversions in the System Niobium-Ruthenium

A. L. TATARINA, V. I. GRYZUNOV, G. N. RONAMI, M. V. RAEVSKAYA, I. G. SOKOLOVA and E. M. SOKOLOVSKAYA, *Vest. Moskov. Univ., Ser. II, Khim.*, 1973, (6), 673-678

Diffusion layer studies at 1000-1700°C on Nb-Ru

alloys and physico-chemical studies on 10% Zr-Nb-Ru alloys at 1050 and 1600°C are reported.

### Intermetallic Compounds in the Ruthenium-Magnesium System

L. WESTIN and L.-E. EDHAMMAR, *Chem. Scripta*, 1973, **3**, (1), 15-22

Phase analysis studies on Mg-rich Ru-Mg alloys show the existence of two cubic phases with homogeneity ranges of  $RuMg_{1.25-2.25}$  and  $RuMg_{6.2-6.6}$ , the former being of the  $\beta$ -Mn type with  $a \approx 6.93\text{Å}$ , while  $RuMg_{6.2}$  has a partly disordered structure of the  $Rh_7Mg_{44}$  type with  $a \approx 20.2\text{Å}$ .

## CHEMICAL COMPOUNDS

### Gaseous Platinum Chloride

U. WOŚIEWITZ and H. SCHÄFER, *J. Less-common Metals*, 1973, **32**, (3), 389-390

The formation of the gaseous  $Pt_6Cl_{12}$  molecules from Rh-Pt alloys and  $Cl_2-N_2$  mixtures was studied at various temperatures and pressures.

### Identification of a Mixed-valence Triclinic Product Formed by the Partial Bromination of $K_2Pt(CN)_4$

N. J. MINOT, J. H. PERLSTEIN and T. J. KISTENMACHER, *Solid State Commun.*, 1973, **13**, (9), 1319-1323

X-ray diffraction and chemical analysis studies showed that the partial bromination of  $K_2Pt(CN)_4$  results in at least 2 structurally and stoichiometrically different products. Triclinic crystals with Pt-Pt spacing 2.95Å grow from acid aqueous solution and tetragonal phases with Pt-Pt spacing 2.88Å grow from basic solutions.

### Interactions between Polynucleotides and Platinum(II) Complexes

S. WHERLAND, E. DEUTSCH, J. ELIASON and P. B. SIGLER, *Biochem. Biophys. Res. Commun.*, 1973, **54**, (2), 662-668

Reaction of either *cis*- or *trans*- $Pt(NH_3)_2Cl_2$  with poly-adenylic acid in dilute aqueous solution leads to quantitative precipitation of the polymer  $>0.5$ . At  $<0.5$ , intramolecular binding of one Pt to two bases is favoured; at higher Pt:nucleotide ratios, intermolecular cross linking is important and precipitation results. The absence of isomer selectivity in precipitation suggests that biological specificity of the *cis*-isomer results from a process other than cross-linking of polynucleotide strands.

### Crystal Structure of $[XeF_5^+]_2[PdF_6^{2-}]$

K. LEARY, D. H. TEMPLETON, A. ZALKIN, and N. BARTLETT, *Inorg. Chem.*, 1973, **12**, (18), 1726-1730

Structure studies showed that  $[XeF_5^+]_2[PdF_6^{2-}]$  unit cell is orthorhombic with  $a=9.346\text{Å}$

$b = 12.786 \text{ \AA}$ ,  $c = 9.937 \text{ \AA}$ ,  $V = 1122.9 \text{ \AA}^3$ ,  $Z = 4$ , and  $d_c = 3.91 \text{ g/cm}^3$ .

### Crystal Structures of $[\text{XeF}^+][\text{RuF}_6^-]$ and $[\text{XeF}_5^+][\text{RuF}_6^-]$

N. BARTLETT, M. GENNIS, D. D. GIBLER, B. K. MORRELL and A. ZALKIN, *Inorg. Chem.*, 1973, **12**, (8), 1717-1721

Structure studies showed that  $\text{XeRuF}_7$  is monoclinic with  $a = 7.991 \text{ \AA}$ ,  $b = 11.086 \text{ \AA}$ ,  $c = 7.250 \text{ \AA}$ ,  $\beta = 90.68^\circ$ ,  $V = 642.2 \text{ \AA}^3$ ,  $Z = 4$ , and  $d_c = 3.78 \text{ g/cm}^3$ .  $\text{XeRuF}_{11}$ , however, is orthorhombic with  $a = 16.771 \text{ \AA}$ ,  $b = 8.206 \text{ \AA}$ ,  $c = 5.617 \text{ \AA}$ ,  $V = 773.03 \text{ \AA}^3$ ,  $Z = 4$ , and  $d_c = 3.79 \text{ g/cm}^3$ .

## ELECTROCHEMISTRY

### The Electro-oxidation of Acetylene on Heterogeneous Au-Pt Alloys

J. W. JOHNSON, C. K. WU and W. J. JAMES, *J. Electrochem. Soc.*, 1973, **120**, (12), 1676-1681

The anodic oxidation of  $\text{C}_2\text{H}_2$  was studied in aqueous solutions at pH 0.3-12.6 at  $80^\circ\text{C}$  on heterogeneous Au-Pt alloy electrodes. Results are interpreted in terms of parallel reactions occurring separately on the Au-rich and Pt-rich phases. The polarisation behaviour on the separate phases is like that of the corresponding pure metals.

### Adsorption Properties of Skeleton Rhodium-Titanium Electrode-catalysts in Relation to Hydrogen in Sulphuric Acid Solutions

G. S. MANANKOVA, G. A. MARTINYUK and G. P. KHOMCHENKO, *Zh. Fiz. Khim.*, 1973, **47**, (12), 3085-3087

Studies of 5, 10, 25, and 40 wt.% Ti-Rh electrode catalysts showed that the adsorption of  $\text{H}_2$  decreases with increasing Ti content until 40% Ti-Rh, when  $\text{H}_2$  adsorption increases again. X-ray studies showed that the main phase is a Rh-based solid solution.

## ELECTRODEPOSITION AND SURFACE COATINGS

### A Study of Contamination on Electroplated Gold, Copper, Platinum, and Palladium

D. L. MALM and M. J. VASILE, *J. Electrochem. Soc.*, 1973, **120**, (11), 1484-1487

Examination of electroplated Au, Cu, Pd and Pt for surface and bulk impurities indicates that electroplated metals have more surface contamination than cast metals after identical cleaning procedures. Methods of removing surface impurities are discussed, whilst bulk impurities are generally indicative of plating bath contamination.

### Reliability in Printed Circuitry Metallisation — A Case for Improved Catalysing Systems

N. FELDSTEIN, *Plating*, 1973, **60**, (6), 611-616

The new approach by which complete metallic

coverage of organic substrates incorporates aged  $\text{SnCl}_2$  solutions with sensitisation by acidic  $\text{SnCl}_2$  and activation by acidic  $\text{PdCl}_2$ , then catalysis with colloidal  $\text{PdCl}_2$  in excess acidic  $\text{SnCl}_2$ .

### The Nucleation with $\text{SnCl}_2$ - $\text{PdCl}_2$ Solutions of Glass before Electroless Plating

G. H. DE MINJER and P. F. J. VAN DER BOOM, *J. Electrochem. Soc.*, 1973, **120**, (12), 1644-1650

Metallic Pd nuclei are formed by the nucleation of nonconducting substrates with  $\text{SnCl}_2$ - $\text{PdCl}_2$ . However, results of experiments on glass using radioactive tracers and ellipsometry showed that no metallic Pd was present after the nucleation.

## LABORATORY APPARATUS AND TECHNIQUE

### Liquid Chemical Products — Measurement of Colour in Hazen Units (Platinum-Cobalt Scale)

*Internat. Std. ISO 2211*, 1973, 2pp

A method of measuring the colour in Hazen (Pt-Co) units of liquid chemical products by visual comparison for routine control.

## HETEROGENEOUS CATALYSIS

### Catalytic Properties of Platinum/Alumina Catalysts Promoted by Rare Earth Elements

N. S. KOZLOV, G. M. SEN'KOV, V. A. POLIKARPOV, V. V. SHIPIKIN and A. M. DAVIDOVSKAYA, *Neftekhimiya*, 1973, **13**, (5), 643-649

Promotion of  $\text{Pt}/\text{Al}_2\text{O}_3$  by Y increases the catalytic activity for dehydrogenation of cyclohexane. 0.1 wt.% of promoter has the greatest effect. During conversion of *n*-octane on the promoted catalyst the aromatics content remains unchanged, but increasing the amount of promoter above 0.1 wt.% depresses the cyclisation capacity of the catalyst. Y improves thermal stability of  $\text{Pt}/\text{Al}_2\text{O}_3$ .

### X-ray Structural Investigation of Platinum/Alumina Catalysts

N. S. KOZLOV, M. YA. LAZAREV, L. YA. MOSTOVAYA and I. P. STREMOK, *Kinet. Kataliz*, 1973, **14**, (5), 1287-1291

$\text{Al}_2\text{O}_3$  and 0.1-3.0 wt.%  $\text{Pt}/\text{Al}_2\text{O}_3$  catalysts studied at  $600$ - $1200^\circ\text{C}$  exhibit the existence of three modifications of  $\text{Al}_2\text{O}_3$ :  $\gamma$ ,  $\theta$  and  $\alpha$ , which are stable over different ranges of temperature. Pt catalyses the conversion of one modification to another.

### Investigation of the State of Platinum in Platinum/Alumina Catalysts for Dehydrocyclisation

N. S. KOZLOV, E. F. IVAN'KOVICH, A. F. VOLKODATOV and G. A. ZHIZHENKO, *Kinet. Kataliz*, 1973, **14**, (6), 1550-1555

Electron microscope studies of  $\text{Pt}/\text{Al}_2\text{O}_3$  with no

Cl<sub>2</sub> but with alkali (K, Cs) and alkaline earth (Ca, Ba) promoters enabled comparisons to be made of Pt crystallite distribution by size and diameter against activity for dehydrocyclisation of *n*-C<sub>6</sub>H<sub>12</sub>. The most active catalysts for this reaction are Pt crystallites of size 40–80Å.

#### Effect of Media on the Intensity of Sintering of Platinum Catalysts

KH. SHPINDLER, I. D. RATNER and L. M. KEFELI, *Kinet. Kataliz*, 1973, 14, (6), 1588–1591

Electron microscope and H<sub>2</sub> adsorption studies of the effect of temperature and the nature of the atmosphere (air, He, vacuum) on the dispersion of Pt in Pt/Al<sub>2</sub>O<sub>3</sub> showed that calcining of the catalyst in air causes a decrease in dispersion by increasing the size of the metal particles.

#### Investigation of Coke Formation during the Aromatisation of Olefins in the Presence of Platinum/Alumina Catalysts

T. V. KURCHATKINA and YU. V. FOMICHEV, *Neftekhimiya*, 1973, 13, (5), 665–668

Studies of coke formation on Pt/Al<sub>2</sub>O<sub>3</sub> during aromatisation of aliphatic olefins show that more coke forms from *n*-C<sub>6</sub>H<sub>12-1</sub> than from *n*-C<sub>7</sub>H<sub>14-1</sub>. Coke formation, determined by catalyst weight increases, rises in the order *n*-C<sub>6</sub>H<sub>12-1</sub> < methylcyclopentane < cyclohexene < methylcyclopentene. Coke yields on Pt/Al<sub>2</sub>O<sub>3</sub> are higher than on halided Al<sub>2</sub>O<sub>3</sub>. Less C<sub>6</sub>H<sub>6</sub> is produced from C<sub>6</sub> olefins than from C<sub>6</sub> paraffins because the rate of deactivation of the catalyst by coke is greater.

#### Effect of Oxygen and Water on the Direction of C<sub>6</sub>-Dehydrocyclisation of *N*-Octane

A. M. GYUL'MALIEV, E. A. UDAL'TSOVA, I. I. LEVITSKII, I. V. STANKEVICH and KH. M. MINACHEV, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1973, (10), 2252–2256

Tests at 450°C, 5 and 20 atm showed that O<sub>2</sub> and H<sub>2</sub>O alter the C<sub>6</sub>-dehydrocyclisation of *n*-octane over 0.3% Pt/Al<sub>2</sub>O<sub>3</sub> in the direction of greater ethylbenzene formation. The electron behaviour during this reaction was investigated. The direction of the reaction depends on the number of electron donors in the Pt after absorption of H<sub>2</sub>O by the catalyst, and on the electron distribution in *n*-octane molecules.

#### Kinetic Study of Carbon Monoxide and Propylene Oxidation on Platinum Catalysts

S. E. VOLTZ, C. R. MORGAN, D. LIEDERMAN and S. M. JACOB, *Ind. Engng. Chem., Prod. Res. Dev.*, 1973, 12, (4), 294–301

The kinetics of CO and C<sub>3</sub>H<sub>6</sub> oxidation on a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst at 400–700°F were studied. Oxidation rate increases with O<sub>2</sub>-concentration but is inhibited by CO, C<sub>3</sub>H<sub>6</sub> and NO. Results obtained are directly relevant to Pt catalytic converters in automobile exhaust emission control systems.

#### Mechanism and Poisoning of the Molecular Redistribution Reaction of Alkanes with a Dual-functional Catalyst System

R. L. BURNETT and T. R. HUGHES, *J. Catalysis*, 1973, 31, (1), 55–64

Alkane disproportionation over Pt/Al<sub>2</sub>O<sub>3</sub> mixed with WO<sub>3</sub>/SiO<sub>2</sub> involves formation of low concentrations of olefin intermediates over the former followed by their disproportionation over the latter. The overall process is better termed molecular redistribution. Straight chain alkanes are more reactive than branched with pure isobutane only slightly reactive. This catalyst system is very sensitive to poisoning by impurities and it must be protected by a suitable guard chamber in the feed line. An excess of olefins or of H<sub>2</sub> over the low intermediate concentrations inhibits the reaction. Catalyst stability is greater at low temperatures and higher pressures, and is also affected by the ratio of Pt/Al<sub>2</sub>O<sub>3</sub> to WO<sub>3</sub>/SiO<sub>2</sub>.

#### Catalysis—Evidence from E.P.R. Is Presented for the Formation of Paramagnetic Platinum by Interaction of Nitric Oxide with Platinum Deposited on Amorphous Alumina

A. GHORBEL, P. MERIAUDEAU and S. J. TEICHER, *Comptes Rend., Sér. C*, 1973, 277C, (17), 739–741

Pt deposited on amorphous Al<sub>2</sub>O<sub>3</sub> shows paramagnetic deviation after adsorption of NO. The conditions for the formation of this paramagnetic Pt, as well as the characterisation of its E.P.R. spectrum at 77K are described and discussed.

#### Effect of Electrolyte Composition on Hydrogen Adsorption by Platinum, Rhodium and Platinum-Rhodium Skeleton Catalysts

T. M. GRISHINA, L. I. LOGACHEVA, V. I. FADEEVA, A. I. STRAT'EV and G. D. VOVCHEV, *Vest. Moskov. Univ., Ser. II, Khim.*, 1973, (5), 586–590

Studies of the effect of electrolyte composition on the H<sub>2</sub> adsorption of Pt metal Raney-type catalysts showed that their ability to adsorb H<sub>2</sub> increases as the content of Rh compared to Pt increases in the electrolyte from which the metals are deposited.

#### Heats of Adsorption of Hydrogen on Skeleton Platinum and Rhodium Catalysts in Sulphuric Acid Solutions

T. M. GRISHINA, L. I. LOGACHEVA and G. D. VOVCHEV, *Zh. Fiz. Khim.*, 1973, 47, (11), 2872–2874

Charging curve studies of the adsorption of H<sub>2</sub> on skeleton Pt and Rh catalysts in 1N H<sub>2</sub>SO<sub>4</sub> at 20°C intervals from 20 to 80°C showed that adsorption decreases as temperature increases. Adsorption isotherms were plotted, the effect of heterogeneity of the surfaces was calculated, and heats of adsorption and energy of bonding of H<sub>2</sub> to the surface were determined.

### Changes in the Morphology of Platinum Agglomerates during Sintering

K. KINOSHITA, K. ROUTSIS, J. A. S. BETT and C. S. BROOKS, *Electrochim. Acta*, 1973, 18, (12), 953-961

Pt black was sintered at 150°C in 96% H<sub>3</sub>PO<sub>4</sub> at various potentials, and the surface area and particle size of the blacks were measured, and any morphological changes were noted. Results indicate that the loss of surface area is accompanied by densification of the agglomerates. Pore size distribution measurement confirmed that pore volume decreases and small pores <10Å are preferentially eliminated; there is also some evidence that some occlusion of pores may occur.

### The Mechanism of Aromatisation on Platinum Black Catalyst; Dehydrocyclisation of Hexadienes and Hexatrienes

Z. PAÁL and P. TÉTÉNYI, *J. Catalysis*, 1973, 30, (3), 350-361

Studies of aromatisation of hexadiene isomers and of *trans*- and *cis*-1, 3, 5-hexatriene on Pt black in He and H<sub>2</sub>-He mixtures showed C<sub>6</sub>H<sub>6</sub> formation in all cases to be of the same order of magnitude. Catalyst activity rapidly decreased when successive pulses of hydrocarbons were introduced without regeneration. *Cis*-1, 3, 5-hexatriene was the exception—C<sub>6</sub>H<sub>6</sub> yield was higher and deactivation was slower. Even small amounts of H<sub>2</sub> slowed the deactivation. The reaction involves dehydrogenation followed by *cis-trans* isomerisation. These processes are equally important but ring closure is very fast. *Trans*-polyenes are precursors of coke formation on the catalyst surface. H<sub>2</sub> in the gas phase determines the relative importance of C<sub>6</sub>H<sub>6</sub> and coke formation.

### Propylene Hydrogenation over Platinum/Carbon Molecular Sieve Catalysts

D. L. TRIMM and B. J. COOPER, *J. Catalysis*, 1973, 31, (2), 287-292

Studies were made of the kinetics of hydrogenation of propylene over Pt/C molecular sieve catalyst and the rates of adsorption and diffusion of reactants and products in the catalyst was found to be a controlling influence on the kinetics.

### On the Connection of the Direction of Hydrogenolysis of Ethylcyclopentane with Its Electronic Structure

A. M. BOGANOV, A. M. GYUL'MALIEV, I. I. LEVITSKII, KH. M. MINACHEV and I. V. STANKEVICH, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1973, (10), 2257-2260

As p<sub>H<sub>2</sub></sub> rises from 0.8 to 7.8 atm the direction of hydrogenolysis of ethylcyclopentane over 20% Pt/C at 250°C changes to give more breakage of bonds adjacent to the ethyl group. The electronic behaviour during such reactions was studied. The direction of the catalysed reaction is related to the electronic structure of the reacting molecule and the catalyst.

### Hydrogenolysis of Spiro[2, 3]hexane on Platinised Kieselguhr

N. S. NAMETKIN, V. M. VDOVIN, E. SH. FINKEL'SHTEIN, A. M. POPOV and A. V. EGOROV, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1973, (12), 2806-2807

Hydrogenolysis of spiro[2, 3]hexane on 15% Pt/kieselguhr at 100°C in a flowing system led to the formation of *gem*-dimethylcyclobutane but at 140-150°C the main substance formed was ethylcyclobutane.

### Influence of the Conditions on the Rate of Conversion of Anatase to Rutile

V. I. BYSTROV, V. V. AVKSENT'EV and V. A. SOKOLOV, *Zh. Fiz. Khim.*, 1973, 47, (10), 2561-2564

X-ray studies of the phase composition of TiO<sub>2</sub> in powder form and as a thin layer on the surface on Ti membranes showed that the ratio rutile:anatase depends on the conditions of TiO<sub>2</sub> formation and on the duration of exposure at different temperatures. Addition of Pt group metal compounds, e.g. RuO<sub>2</sub> and PdO, accelerates the conversion of anatase to rutile.

### Hydrogenation of Alkyl-substituted Naphthalenes over Palladium

T. J. NIEUWSTAD, P. KLAPWIJK and H. VAN BEKKUM, *J. Catalysis*, 1973, 29, (3), 404-411

The kinetics of the hydrogenation of a series of alkyl- and dialkyl-naphthalenes over Pd/C in CH<sub>3</sub>COOH was studied at 80°C and atmospheric pressure. The mechanism of H<sub>2</sub> addition was also discussed. Competitive hydrogenations showed that bulky alkyl substituents reduce absorption.

### On the Stereoselectivity of Heterogeneous Catalysts, Modified by Optically Active Polyelectrolytes

V. K. LATOV, V. M. BELIKOV, K. K. BABIEVSKII and A. I. VINOGRADOVA, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1973, (12), 2764-2770

Optically active phenylalanine was formed during hydrogenation of the methyl ether of  $\alpha$ -acetaminocinnamic acid over Pd black and Raney Ni modified by optically active styrene copolymers with alanine maleimide. The pH of the modifier of Pd black affects both the size and the direction of rotation of the phenylalanine. The size and type of stereoselectivity of the catalysts is related to pH of the modifier by complexes formed on the catalyst surface due to configurational changes of the optically active polyelectrolytes related to the stage of their dissociation.

### On the Effects of Ultraviolet and Visible Light on the Catalytic Oxidation of CO on Pd, Pt and Ag

A. V. SKLYAROV, A. G. VLASENKO and I. I. TRET'YAKOV, *Zh. Fiz. Khim.*, 1973, 47, (11), 2894-2895

The observed increase in the rate of oxidation of

CO by O<sub>2</sub> over Pt and Pd during exposure to UV and visible light is connected only with the initial heating of the catalysts. In the case of Ag, no reaction is observed either during exposure to or absence of light.

#### Conversion of *n*-Heptane during Reaction with Water Vapour on Rhodium/Alumina Catalyst

G. L. RABINOVICH, L. M. TREIGER and G. N. MASLYANSKII, *Neftekhimiya*, 1973, **13**, (5), 659-664  
Both conversion of *n*-C<sub>7</sub>H<sub>16</sub> and its dehydrocyclisation occur during passage of *n*-C<sub>7</sub>H<sub>16</sub> and H<sub>2</sub>O vapour over 0.6% Rh γ-Al<sub>2</sub>O<sub>3</sub>; the ratio of these processes at 430-480°C is 3.0-3.5. Product yields are determined by the depth of conversion of the initial hydrocarbon. The yield of C<sub>6</sub>H<sub>6</sub> significantly exceeds that of C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> because the latter is dealkylated without intermediate desorption.

#### Effect of Carbon Monoxide on the Selectivity of Dealkylation of Toluene on Rhodium Catalyst

L. M. TREIGER, G. L. RABINOVICH and G. N. MASLYANSKII, *Kinet. Kataliz*, 1973, **14**, (6), 1582-1584

Studies of dealkylation and decomposition of toluene over 0.6% Rh/Al<sub>2</sub>O<sub>3</sub> at 430°C, atm. pressure showed that, as CO is introduced up to CO: toluene=0.33, the decomposition is strongly retarded while the reduction in dealkylation is insignificant. CO also retards the decomposition of C<sub>6</sub>H<sub>6</sub> reacted with H<sub>2</sub>O vapour.

#### Hydroformylation of Methyl Oleate with a Recycled Rhodium Catalyst and Estimated Costs for a Batch Process

J. P. FRIEDRICH, G. R. LIST and V. E. SOHNS, *J. Am. Oil Chem. Soc.*, 1973, **50**, (11), 544-548

Methyl oleate was hydroformylated to methyl formylstearate at 120°C, 850-900 p.s.i.g. with a 1:1 mixture of H<sub>2</sub> and CO. In the presence of triphenylphosphine, an activated Rh/Al<sub>2</sub>O<sub>3</sub> catalyst produced essentially quantitative conversion in 40 min. Preliminary processing costs based on a hypothetical plant are given.

#### The Catalytic Hydrogenation of Substituted 4-Chromanones and 4-Chromanols

J. A. HIRSCH and G. SCHWARTZKOPF, *J. Org. Chem.*, 1973, **38**, (20), 3534-3536

Hydrogenations over 5% Ru/C of 6- and 7-carbomethoxy-4-chromanones, 6-methyl-4-chromanone, 6-carbomethoxy-4-chromanol, and the ethylene ketal of 6-carbomethoxy-4-chromanone showed that there are conditions for which the ketones have perhydro alcohols as the major products. Electron donating ring substituents seemed to minimise significantly any competing hydrogenolyses.

#### Synthesis of Polymethylene from Carbon Monoxide and Hydrogen

H. PICHLER and F. BELLSTEDT, *Erdöl Kohle*, 1973, **26**, (10), 560-564

Temperatures of 100-120°C and pressures of 1000-2000 atm were used in the synthesis of polymethylene from CO and H<sub>2</sub> in the presence of Ru catalysts, the activity of which was increased by H<sub>3</sub>PO<sub>4</sub> treatment to produce large amounts.

#### Relation of the Catalytic Activity of Palladium-Ruthenium Alloys to Their Composition and Conditions of Heat Treatment

E. V. KHRAPOVA, V. M. GRYAZNOV, V. I. KALUGA, N. R. ROSHAN, V. I. SHIMULIS, B. DZHUNTINI and V. V. KORNILOV, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1973, (11), 2431-2436

Studies of the heat treatment of 4.4-9.2% Ru-Pd alloys in air, H<sub>2</sub> and Ar showed that raising the temperature from 350 to 750°C during treatment in air and also repetition of this treatment in air at 750°C produces greater catalytic activity, connected with a rise in the pre-exponential factor. Yet more activity caused by a fall in the activation energy is obtained by treatment with air followed by H<sub>2</sub> and then fast cooling in H<sub>2</sub>.

#### The Catalytic Reduction of Nitric Oxide over Supported Ruthenium Catalysts

K. C. TAYLOR and R. L. KLIMISCH, *J. Catalysis*, 1973, **30**, (3), 478-484

Studies of Ru/Al<sub>2</sub>O<sub>3</sub> or Ru/SiO<sub>2</sub> spheres as catalysts for NO reduction in simulated exhaust gases showed that the rate and temperature of NO removal depends largely on NO inlet concentration and are independent of the concentration of reducing agents. Selectivity for N<sub>2</sub> formation depends on concentration of reducing agents CO<sub>2</sub> and H<sub>2</sub> as well as NO concentration. No NH<sub>3</sub> intermediate was indicated in the NO→N<sub>2</sub> reduction over Ru. Ru is highly selective for this reaction because CO inhibits NO reduction over Pt and Pd but not over Ru.

## HOMOGENEOUS CATALYSIS

#### Complex Metal-Polymer Catalysts for Benzene Hydrogenation

E. N. RASADKINA, A. T. TELESHEV, I. D. ROZHDESTVENSKAYA and I. V. KALECHITS, *Kinet. Kataliz*, 1973, **14**, (5), 1214-1221

Complex organoplatinum hydrogenation catalysts supported on nylon can produce up to 1.5% cyclohexene during gas phase conversion of C<sub>6</sub>H<sub>6</sub> amounting to 15%.

#### Silyl Complexes of Nickel, Palladium and Platinum

D. J. JONES, *Organomet. Compounds*, 1973, **23**, (10), 234-238

Studies of the preparation of organosilicon

compounds in reactions of hydrido-silyl compounds with an olefinic compound in the presence of Ni, Pt, Pd metal complexes and their influence as catalysts in the hydrogenation of disilanes, the exchange of Si-Cl, Si-H atoms in hydrosilylation and polymerisation of acetylenic compounds are discussed.

#### **Palladium(II) Chloride Catalysed Decomposition of Vinyl Acetate in Dry Acetic Acid**

P. M. HENRY, *J. Org. Chem.*, 1973, **38**, (20), 3596-3600

Two regions of kinetic behaviour occur in decomposition of vinyl acetate to give  $\text{CH}_3\text{CHO}$  and  $\text{Ac}_2\text{O}$ ; at low  $\text{Cl}^-$ , high Pd(II) and high vinyl acetate concentration the reaction rate was almost independent of them and addition of  $\text{Ac}_2\text{O}$  depressed the rate only slightly; at high  $\text{Cl}^-$ , low Pd(II) and low vinyl acetate concentrations the kinetic behaviour conventionally follows  $-\text{d}[\text{C}_2\text{H}_3\text{OAc}]/\text{dt} = k[\text{Li}_2\text{Pd}_2\text{Cl}_6][\text{C}_2\text{H}_3\text{OAc}]/[\text{LiCl}]$  and  $\text{Ac}_2\text{O}$  strongly inhibits the reaction. A proposed mechanism includes slow formation of  $\text{H}_2\text{O}$  and  $\text{Ac}_2\text{O}$  without Pd(II) catalysis.  $\text{H}_2\text{O}$  then reacts with vinyl acetate to give  $\text{CH}_3\text{CHO}$  and  $\text{CH}_3\text{COOH}$  in a Pd(II) catalysed reaction. Either  $\text{H}_2\text{O}$  formation or the  $\text{H}_2\text{O}$ -vinyl acetate reaction can be the rate-limiting step.

#### **Effect of Solvents on Isomerisation of Heptene-1 in the Presence of $\pi$ -Complexes of Palladium(II) Chloride**

G. M. PANCHENKOV, G. V. DEMIDOVICH, I. N. KARTSIVADZE and YU. M. ZHOROV, *Neftekhimiya*, 1973, **13**, (5), 650-654

Studies of the effect of solvents on the isomerisation of heptene-1 with complexes of Pd(II) showed that alcohols most effectively accelerate the process; acetone, nitrobenzene and acetic acid have little effect;  $\text{C}_6\text{H}_6$  retards the reaction. Alcohols in the presence of  $\pi$ -complexes of  $\text{PdCl}_2$  encourage the formation of *trans* isomers. Process rates with alcohols increase as the polarisability of the alcohol molecules decreases.

#### **Asymmetric Catalytic Reduction with Transition Metal Complexes. II. Asymmetric Catalysis by a Supported Chiral Rhodium Complex**

W. DUMONT, J.-C. POULIN, T.-P. DANG, and H. B. KAGAN, *J. Am. Chem. Soc.*, 1973, **95**, (25), 8295-8299

An insoluble chiral-polymer-supported Rh complex closely related to the soluble Rh(I)-diop complex (diop=2, 3-o-isopropylidene-2, 3-dihydroxy-1,4-bis(diphenylphosphino) butane) was prepared using a Merrifield resin. Synthesis of this catalyst and its use in heterogeneous asymmetric catalysis involving Rh complexes are discussed.

#### **Selective Hydroformylation of Unsaturated Fatty Acid Esters**

E. N. FRANKEL, *Ann. N. Y. Acad. Sci.*, 1973, **214**, 79-93

The preparation and use of  $\text{Rh-Ph}_3\text{P}$  catalyst for the selective hydroformylation of fatty acid esters and its use in hydroformylation of Me oleate, linseed oil and safflower oil was discussed.

#### **Selective Hydrogenation of the Cyclohexadienes Catalysed by *trans*- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$**

J. E. LYONS, *J. Catalysis*, 1973, **30**, (3), 490-494  
*Trans*- $\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2$  catalyses hydrogenation of isomeric cyclohexadienes smoothly and selectively under mild conditions to give predominantly cyclohexene, and little or no isomerisation or disproportionation. Deuteration studies established the reaction mechanism.

#### **Synthesis and Catalytic Properties of Some Carbonyltriphenylphosphineruthenium(II) Complexes**

B. J. JAMES, L. D. MARKHAM, B. C. HUI and G. L. REMPEL, *J. Chem. Soc., Dalton Trans.*, 1973, (21), 2247-2252

$[\text{HRuCl}(\text{CO})_2(\text{PPh}_3)_2]$ ,  $[\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2]$ ,  $[\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2]$ , and  $[\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2\text{L}]$  complexes were prepared from  $[\text{RuCl}_2(\text{PPh}_3)_3]$ . Analogous bromo-complexes were also synthesised. Solvent molecules ( $\text{L}=\text{NN}'$ -dimethylformamide,  $\text{NN}'$ -dimethylacetamide, or dimethyl sulphoxide) are co-ordinated to the metal through O, and are removed by recrystallisation from  $\text{CH}_2\text{Cl}_2$ - $\text{CH}_3\text{OH}$ . Under mild conditions these complexes show low activity for olefin hydrogenation and are ineffective for hydroformylation but  $[\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2]$  is an efficient olefin isomerisation catalyst.

#### **Reduction of Ketones by Secondary Alcohols Catalysed by Triphenylphosphine Complexes of Ruthenium and Rhodium**

V. Z. SHARF, L. KH. FREIDLIN and V. N. KRUTHI, *Izv. Akad. Nauk S.S.S.R., Ser Khim.*, 1973, (10), 2264-2267

The rate of reduction of cyclohexanone by alcohols in the presence of  $\text{RuCl}_2(\text{PPh}_3)_3$  is not related to the length of the alkyl chains in  $\text{C}_4$ - $\text{C}_{11}$  secondary alcohols, or to the presence of secondary butyl or cyclohexyl radicals, but falls sharply during transition to 3-, 4- and 5-alcohols and 3,3-dimethyl-2-butanol. Alkylphenylcarbinols reduce ketones faster than do secondary alcohols and promote conversion of the latter.  $\text{RuCl}_2(\text{PPh}_3)_3$  catalyses ketone reductions by alcohols in descending rates: cyclohexanone > acetophenone > cyclopentanone > 2-hexanone > cycloheptanone > cyclooctanone.  $\text{RhCl}(\text{PPh}_3)_3$  has greater activity for H transfer than  $\text{RuCl}_2(\text{PPh}_3)_3$ ; on it the rate of reaction is scarcely related to alcohol or ketone structure.

## CHEMICAL TECHNOLOGY

### Electrolytic Preparation of Highly Dispersed Pd-Ag Powders of Predefined Chemical Composition

B. P. YUR'EV and S. P. SHKURYAKOVA, *Porosh. Metall.*, 1973, 13, (6), 6-10

X-ray studies were made on highly dispersed Ag-Pt powders obtained electrolytically from  $\text{NH}_3$  solution with Pt and Ag nitrates and on the effect of different electrolysis parameters on their current yields, chemical compositions and dispersion.

## DENTAL AND MEDICAL USES

### Towards a Dosimetric System for Use with Iridium-192 Wires in Interstitial Therapy: a Suggested Protocol for Planning the Single Plane Implant

A. WAMBERSIE and A. DUTREIX, *Atomkern. Energie*, 1973, 22, (2), 134-138

The results of a dosimetric study for planning single plane implants of parallel equidistant Ir-192 wires are described. Dose distributions were computed for different arrangements of wires.

## NEW PATENTS

### METALS AND ALLOYS

#### Internal Oxidation of Work-hardened Platinum and Gold and Alloys thereof

JOHNSON, MATTHEY & CO. LTD.

*British Patent* 1,340,076

Pt-group metals and alloys thereof are dispersion-strengthened by alloying with up to 5 wt.% of a material capable of forming a stable, refractory oxide, flame-spraying the alloy into water to form granules, ball-milling and recrystallising the granules and then internally oxidising prior to compacting and sintering.

#### Ball Point Pen Writing Ball

THE PARKER PEN CO. *U.S. Patent* 3,746,456

Cemented carbide compositions to make ball points are produced from WC or TiC and a binder alloy containing Co and Ni, and ~18-20% Cr, 0.1-1% Pt and 0-3% Fe.

#### Cobalt-Platinum Group Alloys Whose Anisotropy Is Greater than Their Demagnetisable Field

INTERNATIONAL BUSINESS MACHINES CORP.

*U.S. Patent* 3,755,796

These alloys contain not less than 50% Co and the balance in the form of Ru, Re, Os, Rh, Ir, Si, Ge, As and/or Pt able to depress the saturation magnetisation field of the Co.

### CHEMICAL COMPOUNDS

#### Synthesis of Silylmetallic Complexes

DOW CORNING CORP. *U.S. Patent* 3,746,732

Silyl complexes of Pt and Pd are prepared by reacting below 150°C, disilanes or hydrosilanes with phosphine complexes of the formula  $\text{M}(\text{PR}'_3)_2\text{Y}_2$ . Specifically, hexachlorodisilane is reacted with  $\text{Pd}(\text{PPhMe}_2)_2\text{Cl}_2$  to give  $\text{Pd}(\text{PPhMe}_2)_2(\text{SiCl}_3)\text{Cl}$  and/or  $\text{Pd}(\text{PPhMe}_2)_2(\text{SiCl}_3)_2$ .

### ELECTROCHEMISTRY

#### Electrolysis Electrodes

ELECTRONOR CORP. *British Patent* 1,344,241

A new electrode coating consists of a coherent mixture of cobalt titanate and a valve metal oxide-precious metal oxide solid solution, e.g. a  $\text{TiO}_2$ -RuO<sub>2</sub> solid solution.

#### Brine Electrolysis Electrode

CHEMNOR A.G. *U.S. Patent* 3,751,296

An electrically conducting base is coated with a mixed crystal material formed from a film-forming metal oxide and a Pt-group metal oxide to form a brine electrolysis electrode. Ru and Ti oxides are suitable materials.

#### Brine Electrolysis Anode

PROGIL *U.S. Patent* 3,763,005

The cell has a cationic permselective membrane placed between a porous anode of the Ti-group having a Pt-group metal coating on the surface opposite the membrane and the cathode.

### ELECTRODEPOSITION AND SURFACE COATINGS

#### Metallisation of Plastics

IMPERIAL CHEMICAL INDUSTRIES LTD.

*British Patent* 1,335,962

Substrates to be chemically plated may be treated with an organic cation solution and then with a Pt-group metal solution to complete the sensitisation.

#### Electroless Deposition of Palladium Alloys

U.S. SECRETARY OF THE ARMY

*U.S. Patent* 3,754,939

The constituents for a plating solution for providing a low porosity electroless deposit of Pd alloys