

# ABSTRACTS

## *of current literature on the platinum metals and their alloys*

### PROPERTIES

#### High Temperature Creep of 40% Rh-Pt Alloy

V. I. SHALAEV, I. B. TRACHENKO, V. P. KETOVA and V. A. PAVLOV, *Fiz. Metal. Metalloved.*, 1974, **38**, (4), 827-833

Creep tests on 40 wt.% Rh-Pt in vacuum at 1160-1750°C with applied stresses of from 0.5 to 6.0 kg/mm<sup>2</sup> showed that the alloy behaves similarly to the pure metals.

#### Low Temperature Thermophysical and Mechanical Properties of High Purity Platinum-25 w/o Iridium Alloy

R. J. FOLEY and F. J. JELINEK, *U.S. Rept. UCRL-75278*, 1974, (Feb.), 8 pp.

The low temperature properties of 25%Ir-Pt alloy were studied at 4-300K using a fused silica dilatometer. The values of thermal contraction and conductivity, as well as tensile strength at 300 K and 20 K are given.

#### Influence of Thermomechanical Treatment on the Tensile Properties of a Platinum-25 wt.% Iridium Alloy

R. J. FOLEY, G. S. ROOT, J. R. HAUBER, D. P. MOAK and W. H. PFEIFER, *U.S. Rept. UCRL-75630*, 1974, 18 pp.

25% Ir-Pt alloys, synthesised by arc melting and hot worked at 1343°C, were tensile tested under two different conditions of cold work following a water quench from the hot-work temperature. Results show an absence of work hardening and a significant reduction in yield strength with increasing cold work and, by adding an ageing step of 5 h at 700°C, significant strength increases were obtained. The maximum strength for 25% Ir-Pt alloy was achieved by series of cold-work and ageing operations.

#### Elastic Constants of Fe-Pt Alloys. I. Single Crystalline Elastic Constants of Fe<sub>72</sub>Pt<sub>28</sub>. II. Young's Modulus of Fe-Pt (25-29%Pt)

G. HAUSCH, *J. Phys. Soc. Japan*, 1974, **37**, (3), 819-823, 824-827

The elastic constants  $C_L$  of a disordered Fe<sub>72</sub>Pt<sub>28</sub> single crystal measured as a function of temperature show that  $C_L$  goes through a minimum at 50°C and that a magnetically induced reduction is present up to 200°C above  $T_C$ . Results are also presented for the temperature dependence of Young's modulus of 25-29% Pt-Fe alloys in the ordered and disordered states.

#### Platinum Silicide Formation: Electron Spectroscopy of the Platinum-Platinum Silicide Interface

S. DANYLUK and G. E. MCGUIRE, *J. Appl. Phys.*, 1974, **45**, (12), 5141-5144

Electron spectroscopy studies were made of the interface between the Pt metal and PtSi formed by d.c. sputtering and filament evaporation. The results show that, after sintering in N<sub>2</sub>, the PtSi is separated from Pt metal by a "protective" layer identified as PtSiO<sub>4</sub>. This layer has a significantly slower etch rate in standard etchants than Pt metal and PtSi, and is formed during sintering by an interaction between Pt metal and SiO<sub>2</sub>.

#### On the Constitution of the Mixture Platinum-Gallium and Platinum-Gallium-Germanium

T. CHATTOPADHYAY, K. KHALAFF and K. SCHUBERT, *Metall*, 1974, **28**, (12), 1160-1168

Phases Pt<sub>0.62</sub>Ga<sub>0.32</sub>, Pt<sub>2</sub>Ga.h, Pt<sub>2</sub>Ga.r, Pt<sub>6</sub>GaGe, and Pt<sub>4</sub>GaGe were studied and their crystal structures were determined.

#### Initial Sintering of Palladium Powder Compacts

H. U. ANDERSON, *Sci. Sintering*, 1974, **6**, (1), 45-58

Compacts of 0.06 μ Pd powder vacuum sintered at 300-550°C showed shrinkage kinetics which agree with a model based on grain boundary diffusion. Spherical Pd powder 60-525 μ was sintered at 1510°C in air. The initial sintering kinetics correlate well with volume diffusion kinetics.

#### Effect of Short Range Order on Mechanical Properties of Alloys

M. E. NICHOLSON, *U.S. Rept. COO-1009-10*, 1974, 8 pp.

Study was made of the anomalous electrical resistivity behaviour of Ag-Pd and Au-Pd alloys on cold working and annealing. The anomalous behaviour was explained on the basis that cold working destroyed short range order.

#### Concentration Dependence of the Superconducting Transition Temperature in PdH<sub>x</sub> and PdD<sub>x</sub>

J. E. SCHIRBER and C. J. M. NORTHROP, *Phys. Rev. B*, 1974, **10**, (9), 3818-3820

Studies of an inverse isotope effect between homogeneous bulk PdH<sub>x</sub> and PdD<sub>x</sub> showed that maximum x values achieved by high-pressure charging were 0.99 and 0.97 for the hydride and

deuteride, respectively. Extrapolated values for the superconducting transition temperature of PdH and PdD are 8 and 10 K, respectively.

### Absorption of Hydrogen by Substitutional fcc Lead/Palladium Alloys

K. D. ALLARD, J. F. LYNCH and T. B. FLANAGAN, *Z. Phys. Chem. (Frankfurt)*, 1974, **93**, (1-6), 15-32  
Studies of the H absorption of a series of substitutional f.c.c. Pb-Pd alloys show that the relative partial molar enthalpies of absorption at infinite dilution decrease with Pb content of the alloys. Lattice parameters of the H-containing alloys showed that the second,  $\beta$ -phase, does not form at substitutional Pb contents  $> 8.5$  at.% (298 K).

### Study of the Kinetics and Mechanism of the Strengthening of Mn-Pd Alloys

M. P. RAYDEL' and O. I. EVDOKIMOVA, *Metalloved. Term. Obrab. Metal.*, 1974, (11), 53-57  
Studies of the  $\gamma$ -Mn phase of 5, 10, 15, 20, 30 and 66% Pd-Mn alloys during their annealing for 1-10 min at 450-600°C in HCl show that 30% Pd-Mn alloy has the highest strengthening coefficient and good corrosion properties.

### An Investigation of the Structure of Pd<sub>2</sub>Si Formed on Si

S. S. LOU and D. SIGURD, *J. Electrochem. Soc.*, 1974, **121**, (11), 1538-1540  
Studies of the structure of the as-deposited Pd films and the silicide films formed on Si substrates of various orientations, and their possible relationship with the transformation kinetics of the Pd<sub>2</sub>Si phase showed that the lattice diffusion of materials through the Pd<sub>2</sub>Si layer is the rate-controlling step for Pd<sub>2</sub>Si formation.

### Thermodynamic Considerations on the Formation and Stability of Metallic Glasses

H. S. CHEN, *Acta Metall.*, 1974, **22**, (12), 1505-1511  
The formation and stability of metallic glasses of compositions  $(Pd_{1-x}M_x)_{0.835}Si_{0.165}$   $(Pd_{1-x}T_x)_{1-xp}P_{xp}$  and  $(Pt_{1-x}Ni_x)_{1-xp}P_{xp}$  were studied (where T=Ni, Co and Fe and M=Rh, Au, Ag, Cu, and T). The results show that the admixture of metallic elements of different atomic sizes and strong atomic interactions, which lowers the melting temperature and raised the glass temperature, facilitates the formation of glasses.

### Thermal Expansion and Density of Glassy Pd-Ni-P and Pt-Ni-P Alloys

H. S. CHEN, J. T. KRAUSE and E. A. SIGERY, *J. Non-cryst. Solids*, 1973-74, **13**, (2), 321-327  
The thermal expansion and density of  $(Pd_{1-x}Ni_x)_{0.80}P_{0.20}$  and  $(Pt_{1-y}Ni_y)_{0.75}P_{0.25}$  alloys were measured from room temperature to the glass transition temperature  $T_g$ . The thermal expansion of the glassy alloys at room temperature varies linearly with x and y and is 10-20% higher than that of the corresponding pure metals.

### Debye Temperature in Noble Metals

K. L. NARAYANA and K. M. SWAMY, *Mater. Sci. Engng.*, 1975, **18**, (1), 157-158  
The longitudinal and transverse sound velocities and Debye temperatures ( $\theta_D$ ) were calculated for Au, Ag, Pt, Pd, Ir, Rh, Os, and Ru using their elastic properties. Values of  $\theta_D$  for Au, Ag, Pt, Pd, Ir, Rh, Os, and Ru; 164 K, 226 K, 240 K, 300 K, 420 K, 480 K, 500 K, and 600 K respectively, were obtained by calorimetric measurements in the liquid-He range or lower.

### The Low Temperature Resistivity of RhFe

R. L. RUSBY, *J. Phys. F: Metal Phys.*, 1974, **4**, (8), 1265-1274  
Measurements of the resistivity of 0.004-2.2 at.% Fe-Rh alloy at 0.5-30 K showed that magnetic ordering to a spin glass state takes place at low temperatures in alloys containing more than 5% Fe, while at lower concentrations the ground state is nonmagnetic.

### Magnetic and Superconducting Properties of the System Mo<sub>77</sub>Ir<sub>23-x</sub>Fe<sub>x</sub>

Ø. FISCHER, A. TREYVAUD, G. BONGI, H. JONES and R. FLÜKIGER, *J. Phys. F: Metal Phys.*, 1974, **4**, (8), 1187-1203  
Studies show that Fe is magnetic when introduced as an impurity in the A15 super-conductor Mo<sub>77</sub>Ir<sub>23</sub>. The superconducting properties are explained in terms of standard pair breaking theories including a negative exchange field and the effects of the short range ordering.

### Cemented Carbides with High-melting-point Precious Metal-binder Phase

J. S. JACKSON, R. WARREN and M. B. WALDRON, *Powder Metallurgy*, 1974, **17**, (34), 255-270  
Studies of alloy systems consisting of TiC and WC in combination with Ru and Ru-Pd alloys show that in TiC-(Ru, Ni) alloys a small amount of Ni required for effective sintering does not affect the properties of the alloys and that, with this quantity of Ni, the melting point of the binder phase is still significantly higher than that of conventional cemented carbides.

## CHEMICAL COMPOUNDS

### Interaction of Platinum Compounds with Dinucleotides

I. A. G. ROOS, A. J. THOMSON and S. MANSY, *J. Am. Chem. Soc.*, 1974, **96**, (20), 6484-6491  
Spectroscopic studies of the interaction of a number of Pt complexes with the dinucleotide A3'p5'A, A2'p5'A, A3'p5'C, A2'p5'C, and A3'p5'U showed the possibility of a metal ion being chelated to form an interbase link within the dinucleotide. *cis*-Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and *cis*-Pt(enim)<sub>2</sub>Cl<sub>2</sub> (enim=ethylenimine) form an interbase link with A3'p5'A and A3'p5'C,

whereas *trans*-Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> reacts only to bring about unstacking of the dinucleotides.

### New Structural Findings from a Neutron Diffraction Study of One-dimensional K<sub>2</sub>Pt(CN)<sub>4</sub>Br<sub>0.3</sub>·3H<sub>2</sub>O

J. M. WILLIAMS, J. L. PETERSEN, H. M. GERDES and S. W. PETERSON, *Phys. Rev. Lett.*, 1974, **33**, (18), 1079-1081

Single-crystal neutron-diffraction structure studies of K<sub>2</sub>Pt(CN)<sub>4</sub>Br<sub>0.3</sub>·3H<sub>2</sub>O showed it to be noncentrosymmetric (space group P4<sub>mm</sub>). The Pt(CN)<sub>4</sub><sup>-2</sup> groups are not precisely planar, the K<sup>+</sup> ions occupying ordered sites, and two crystallographically different Br<sup>-</sup> ion sites are observed.

### The Crystal Structure of Pd<sub>9</sub>P

Y. ANDERSSON, V. KAEWCHANSILP, M. DEL ROSARIO CASTELEIRO SOTO and S. RUNDQVIST, *Acta Chem. Scand.*, 1974, **A28**, (7), 797-802

X-ray diffraction studies of the crystal structure of Pd<sub>9</sub>P showed it to be monoclinic with *a* = 2.837, *b* = 9.441, *c* = 7.695 Å and β = 90.20°. The structure is closely related to the Re<sub>3</sub>B-type structure.

### The Structure of PdPS and the Crystal Chemistry of Late Transition-metal Dipnictides and Dichalcogenides

W. JEITSCHKO, *Acta Cryst. B*, 1974, **30**, (11), 2565-2572

Crystal studies of PdPS showed it to be orthorhombic with *a* = 13.3045, *b* = 5.6777, *c* = 5.6932 Å and *Z* = 8; PdPS forms double nets, thus combining bonding characteristics of PdP<sub>2</sub> and PdS<sub>2</sub>.

## ELECTROCHEMISTRY

### A Palladium Hydride pH Electrode for Use in Buffered Etch Solutions

R. JASINSKI, *J. Electrochem. Soc.*, 1974, **121**, (12), 1579-1584

Lifetime of Pd electrodes cathodically charged to Pd hydride and stability in NH<sub>4</sub>F, as well as in NH<sub>2</sub>SO<sub>4</sub>, pH 3.6 Na citrate and in pH 8 (NH<sub>4</sub>)<sub>2</sub>PO<sub>4</sub> are increased by maximising Pd hydride concentration and the electrode volume. Electrode lifetime was measured for 7-14 days for all solutions, which is the longest time ever reported.

### Dissolution of Palladium in Various Electrolytes

I. N. SOROKIN, A. P. ALEKHIN and V. P. LAVRITSEV, *Zh. Fiz. Khim.*, 1974, **48**, (12), 3067-3070

Potentiodynamic studies of anodic dissolving of Pd powder on sital blocks with a Ti substrate in aqueous KCl, KBr, KNO<sub>3</sub>, and KCNS solutions indicated the effects of concentration, electrolyte temperature and increasing potential on the intensity of the electrode processes. Calculated were the activation energy, the pre-exponential factor and the entropy of Pd ionisation.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Electrodeposition of Palladium-Tin alloy

C. N. VINOGRADOV, N. F. DEDUSHEV, L. P. VERSHININA and G. P. SUVOROVA, *Zashchita Metal.*, 1974, **10**, (5), 601-603

Studies of the microhardness and the contact resistance of Pd-Sn alloys electrodeposited on Pt anode in 20% Pd ethylenediamine and Sn pyrophosphate electrolyte at 50-60°C showed that the best soldering alloy is 15% Pd-Sn with high microhardness and with high contact resistance.

## LABORATORY APPARATUS AND TECHNIQUE

### Rotating Disc Electrode Technique for a Kinetic Study on the Charge Transfer Reaction between Molten Silicate and Solid Platinum at High Temperature

M. KAWAKAMI and K. S. GOTO, *Metall. Trans.*, 1974, **5**, (10), 2244-2246

Detailed studies of rotating disc electrode technique, the rotating electrode made of Pt disc and 13% Rh-Pt wire being used for the thermocouple, were made to find how to apply this technique to the kinetic study on the charge transfer reaction between solid Pt and molten silicates at high temperature.

## HETEROGENEOUS CATALYSIS

### Reaction of Methylcyclopentane and *n*-Hexane over Evaporated Platinum Film Catalysts

J. R. ANDERSON and K. SHIMOMURA, *Bull. Chem. Soc. Japan*, 1974, **47**, (9), 2327-2328

Studies of *n*-hexane and methylcyclopentane reactions over polycrystalline Pt films evaporated in a ultrahigh vacuum condition showed that the initial distribution of reaction products varied with the reaction temperature and the hydrogen/hydrocarbon ratio. The effect of the reaction conditions was interpreted as depending on the possible reaction mechanisms cited.

### Thermal Deactivation of a Platinum Monolithic Carbon Monoxide/Hydrocarbon Oxidation Catalyst

S. E. VOLTZ and D. LIEDERMAN, *Ind. Engng. Chem., Prod. Res. Dev.*, 1974, **13**, (4), 243-250

The thermal deactivation of a Pt monolithic oxidation catalyst was studied at 1400-2400°F. The effects of the thermal treatments on the oxidation of CO, C<sub>3</sub>H<sub>8</sub>, C<sub>3</sub>H<sub>6</sub>, and engine exhaust gas were measured. The catalysts were characterised by measurement of surface area, CO and H<sub>2</sub> chemisorptions, X-ray line broadening, and

X-ray diffraction; scanning electron micrography was used to examine surface morphology. The growth of large Pt crystallites occurred even at 1400°F. Considerable sintering of the Al<sub>2</sub>O<sub>3</sub> washcoat took place above 1800°F, and solid-state phase changes in the ceramic occurred above 2200°F.

### Calculation of the Dispersion of Platinum in Platinum/Alumina Catalysts from Oxygen Chemisorption Data

L. P. MILOVA, N. M. ZAIDMAN, YU. A. SAVOSTIN and R. N. KHARLAMPOVA, *Kinet. Kataliz*, 1974, **15**, (5), 1353-1354

The chemisorption of H<sub>2</sub> on Pt and the dispersion of Pt on Al<sub>2</sub>O<sub>3</sub> are related to the chemisorption of O<sub>2</sub>. The changed stoichiometry of O<sub>2</sub> chemisorption on highly dispersed Pt is considered.

### Increase in the Stability of Platinum Reforming Catalysts by the Addition of Rhenium

B. M. PAVLIKHIN, A. I. PAVLOV and M. E. LEVINTER, *Izv. Vyssh. Ucheb. Zaved., Neft' Gaz*, 1974, **17**, (5), 49-52

Pt, Re and Cl were applied to Al<sub>2</sub>O<sub>3</sub> for aromatisation of *n*-heptane. Re was applied as HReO<sub>4</sub> obtained by dissolving Re in HNO<sub>3</sub>. Catalysts containing 0.45-0.55% Pt, 0.2-0.3% Re and 1.2-1.5% Cl had higher stability and resistance to coking than those containing 0.45-0.6% Pt and 0.35-1.2% Cl.

### Catalytic Radiant Panels at Low Temperature. I. Characteristic Construction and Functioning. II. Preparation and Pretreatment of Structure at High Dispersion of Active Metal on Fibres of Various Types

G. SALVI, E. ZANELLA and G. REZZONICO, *Riv. Combustibili*, 1974, **28**, (10), 349-355, 356-362

Precious metal catalytic radiant flameless heaters operating at low temperature were prepared. Very short preheating time and low unburnt concentrations in gases were achieved with extremely small amounts of Pt/Al<sub>2</sub>O<sub>3</sub> fibre support. Theoretical considerations are reported on the properties of radiant heat transfer of these materials.

### Catalytic Cyclotrimerisation of Ethylene into Benzene

O. V. BRAGIN, A. V. PREOBRAZHENSKII and A. L. LIBERMAN, *Izv. Akad. Nauk S.S.S.R., Ser.Khim.*, 1974, (12), 2751-2757

Calculations of the thermodynamic equilibria of the cyclotrimerisation of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> and of the cyclodimerisation of C<sub>3</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub>, to C<sub>6</sub>H<sub>6</sub> indicated that over a wide range of temperature at atmospheric pressure the reactions 3C<sub>2</sub>H<sub>4</sub> ⇌ C<sub>6</sub>H<sub>6</sub> + 3H<sub>2</sub> and 2C<sub>3</sub>H<sub>6</sub> ⇌ C<sub>6</sub>H<sub>6</sub> + 3H<sub>2</sub> are completely displaced to the right. Five samples of Pt/Al<sub>2</sub>O<sub>3</sub> were studied for activity in cyclotrimerisation of C<sub>2</sub>H<sub>4</sub>; the most active was prepared using fluoride-free Al<sub>2</sub>O<sub>3</sub> modified by

HNO<sub>3</sub> and the yield of aromatics on its reached 11.2% for C<sub>2</sub>H<sub>4</sub> and half as much again for C<sub>3</sub>H<sub>6</sub>. The data agree with the supposition that cyclotrimerisation of C<sub>2</sub>H<sub>4</sub> proceeds via intermediate formation of C<sub>3</sub>-C<sub>6</sub> aliphatic hydrocarbons.

### On Features of the Mechanism of Formation of Cyclopentanes on Platinum/Alumina Catalysts

O. V. BRAGIN, A. V. PREOBRAZHENSKII, I. V. GOSTUNSKAYA, V. G. TOVMASYAN, A. L. LIBERMAN and B. A. KAZANSKII, *Izv. Akad. Nauk S.S.S.R., Ser.Khim.*, 1974, (12), 2746-2751

The conversion of 3-methylpentane to 3-methylpentene-2 at 275-400°C on the bifunctional 0.6% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst was studied and showed that, in a stream of H<sub>2</sub>, cyclisation to methylcyclopentane occurs. C<sub>5</sub>-dehydrocyclisation is presumed to occur by direct alkane-cyclane closure of the C<sub>5</sub> ring.

### Investigation of the Activity of Platinum/Alumina Catalysts with Various Contents of the Metal According to the Model Reaction of the Hydrogenation of Benzene

Z. V. GARIPPOV, F. F. SADYKOV, G. I. FEDOROV and R. I. IZMAILOV, *Neftekhimiya*, 1974, **14**, (6), 834-836

Using vapour-phase hydrogenation of C<sub>6</sub>H<sub>6</sub> as a model reaction, studies showed that catalytic activity of Pt/Al<sub>2</sub>O<sub>3</sub> at 60-110°C depends on the Pt content. Catalytic efficiency is directly proportional to metal content up to 0.6 wt.% Pt but it remains constant above that figure.

### The Effect of Elements of Groups II-IV of the Periodic System on the Properties of Platinum Catalysts on Supports in the Aromatisation of Hydrocarbons

N. R. BURSIAI, S. B. KOGAN, Z. A. DAVYDOVA and A. A. YAKOVLEV, *Kinet. Kataliz*, 1974, **15**, (6), 1486-1488

Additions of MgO, BaO, B<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, Sc<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, and ZrO<sub>2</sub> increase the activity of Pt/SiO<sub>2</sub> in aromatisations of *N*-hexane and of cyclohexane at atm. pressure by slowing down the growth of Pt crystals, corresponding to a change in the content of the soluble form of Pt in the catalysts. These Group III-IV elements also increase the stability of Pt/Al<sub>2</sub>O<sub>3</sub> during heat treatment and oxidative regeneration.

### Investigation of Promoted Platinum-Palladium Catalysts on Silica Supports by the X-ray Structure Method

N. R. BURSIAI, P. P. BOL'SHAKOV and S. B. KOGAN, *Kinet. Kataliz*, 1974, **15**, (5), 1307-1310

Crystal sizes, phase compositions and distribution of crystal phases were determined in Pt-Pd/SiO<sub>2</sub> promoted by oxides of Al, Zr and Ce. The catalysts were treated in air and H<sub>2</sub> at 550°C. No

new phases were formed by promoting additions, only Pt-Pd solid solutions being observed. Unpromoted samples in the amorphous state contain 10% of Pt metals but during promotion this rises to 25-45%.

#### Investigation of the Means of Initiating Liquid-phase Oxidation of Cumene in the Presence of Platinum and Palladium Catalysts

YU. D. NORIKOV and A. L. SMIRNOVA, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1974, (12), 2688-2691  
Chief products of the liquid phase oxidation of cumene in the presence of Pt and Pd blacks, and of Pt and Pd on Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub>, are cumene hydroperoxide, dimethylphenylcarbinol and acetophenone. The rate of oxidation on the supported metals is greater than on the pure metals. Initiation of the processes is connected with the reactions of O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> with the catalysts. Formation of radicals via dehydrogenation of hydrocarbons does not occur.

#### On the Formation of Platinum/Zeolite Catalysts with High Dispersed Metals

A. I. MASHCHENKO, O. D. BRONNIKOV, R. V. DMITRIEV, V. I. GARANIN, V. B. KAZANSKII and KH. M. MINACHEV, *Kinet. Kataliz*, 1974, 15, (6), 1603-1604

The thermal decomposition in vacuum of [Pt(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>, introduced into zeolites by ion exchange, was studied by i.r. spectroscopy and disclosed that (Pt-H)<sup>+</sup> is formed on the surface when reduction by H<sub>2</sub> occurs during heating above 300°C. Treatment in vacuum affects the dispersion of metallic phases after reduction.

#### Crystallite Growth of Platinum Dispersed on Graphitised Carbon Black

J. A. BETT, K. KINOSHITA and P. STONEHART, *J. Catalysis*, 1974, 35, (2), 307-316

The growth of Pt crystallites supported on C during heat treatment was studied in the terms of models assuming surface diffusion of the crystallites (Smoluchowski model) and migration of Pt atoms for the rate determining steps. The studies show that the sintering of Pt/C can be determined in terms of a Smoluchowski mechanism in which crystallites migrate from trap sites on the support and coalesce on the C surface.

#### Hydrogenation of Hexyne-1 on Pt Black under Pressure of Hydrogen in Buffer Solution

A. M. SOKOL'SKAYA, A. UALIKHANOVA and T. OMARKULOV, *Kinet. Kataliz*, 1974, 15, (6), 1599-1601

Studies of the hydrogenation of hexyne-1 on Pt black in universal buffer solution at pH values 2.7, 6.5 and 13.8 showed that the process is not selective and that it is not accompanied by isomerisation or by *cis-trans* conversion.

#### Reactions of Hydrocarbons on Palladium-Gold Alloys

C. VISSER, J. G. P. ZUIDWIJK and V. PONEC, *J. Catalysis*, 1974, 35, (3), 407-416

Studies of Pd and Pd-Au catalysts during the hydrogenation of acetylene and reactions of hexane show that alloying increases the selectivity for nondestructive reactions of hexane, and the activity in hydrogenation of acetylene as a function of alloy composition shows a maximum.

#### Catalytic Reduction. III. Hydrogenation of Unsaturated Compounds over Borohydride Reduced Palladium

T. W. RUSSELL and D. M. DUNCAN, *J. Org. Chem.*, 1974, 39, (20), 3050-3052

Studies of borohydride reduced Pd as a hydrogenation catalyst showed no hydrogenolyses of N and O groups  $\sigma$ -bonded to C in alcohols, amides, amines, esters, ethers, or lactones. Borohydride reduced Pd catalyst was selective in catalysing only the reduction of the N-N  $\pi$  bond in azobenzene.

#### Mechanisms of Isomerisation and Hydrogenolysis of Hexanes on Palladium-Alumina Catalysts

M. HAJEK, S. COROLLEUR, C. COROLLEUR, G. MAIRE, A. O'CONNOR and F. G. GAULT, *J. Chim. Phys.*, 1974, 71, (10), 1329-1336

The isomerisation and hydrogenolysis of methylpentanes, *n*-hexane and methylcyclopentane were studied over 10% Pd/Al<sub>2</sub>O<sub>3</sub> catalyst at 250-350°C. Isomerisation of hexanes occurs according to a cyclic mechanism and is demonstrated by the initial product distributions and by <sup>13</sup>C labelling experiments.

#### Mass Transfer in a Fixed-bed Gas-Liquid Catalytic Reactor with Concurrent Upflow

J. W. SNIDER and J. J. PERONA, *J. Am. Inst. Chem. Eng.*, 1974, 20, (6), 1172-1177

Mass transfer coefficients for the hydrogenation of  $\alpha$ -methylstyrene were measured in a packed-bed reactor with concurrent gas and liquid upflow; the packing in question was 0.29 cm diameter Pd/Al<sub>2</sub>O<sub>3</sub> spheres. Mass transfer coefficients increase as the  $\frac{1}{2}$  power of the liquid rate and increase with gas rate to Reynolds No.  $\approx$  50. The severe decrease for higher gas rates may be due to pulsating flow.

#### The Activation of Palladium Catalysts by Rare Earth and Other Oxides for the Hydrogenation of Cyclohexene

S. M. ISMAIL, M. A. ALBEM and A. ALI, *Rev. Roum. Chim.*, 1974, 19, (5), 847-857

Studies of the activation of Pd catalysts by rare earth and other oxides made during hydrogenation of cyclohexane in EtOH at 1 atm and 30°C showed that the effect of promoting the catalytic activity

of Pd decreased in the order:  $\text{ThO}_2 > \text{ZrO}_2 > \text{Cr}_2\text{O}_3 > \text{CeO}_2 > \text{TiO}_2 > \text{V}_2\text{O}_5 > \text{La}_2\text{O}_3 > \text{Pr}_6\text{O}_{11} > \text{Tl}_2\text{O}_3 > \text{Sm}_2\text{O}_3$ . Activation energies observed were higher for the promoted catalysts than for reduced Pd.

### Hydrogenation of 2-Methylpentene-2 over Palladium Catalyst

N. N. KHOR'KOVA, A. D. BERENTS, A. B. VOL'-EPSHTEIN, S. G. GAGARIN and A. A. KRICHKO, *Neftekhimiya*, 1974, **14**, (6), 828-833

Studies of the kinetics of the conversion of 2-methylpentene-2 over PdS at  $p_{\text{H}_2} = 30$  atm, 75-125°C enabled the rate constants of isomerisation and of hydrogenation to be determined. The limiting stage in the formation of saturated compounds is the reaction of olefins with the catalyst.

### Conversion of Alcohols into Unsymmetrical Secondary or Tertiary Amines by a Palladium Catalyst. Synthesis of N-substituted Pyrroles

S.-I. MURAHASHI, T. SHIMAMURA and I. MORITANI, *J. Chem. Soc., Chem. Commun.*, 1974, (22), 931-932  
The Pd-induced reaction of arylmethanols or allyl alcohols with amines provides a useful method for synthesis of secondary or tertiary amines. N-substituted pyrroles can be prepared by the Pd-catalysed reaction of but-2-ene-1, 4-diol with primary amines in excellent yields.

### Adsorption and Catalytic Properties of Rhodium

G. D. ZAKUMBAEVA, L. A. BEKETAEVA and D. V. SOKOL'SKII, *Internat. Chem. Engng.*, 1974, **14**, (4), 679-686

Experimental results on the adsorption of  $\text{H}_2$ , propargyl alcohol, allyl alcohol, dimethylethynyl carbinol and dimethylvinylcarbonyl on Rh are presented as a function of temperature, concentration of the organic compound in solution and Rh potential.

### Reactions of Alkanes on Iridium-Gold Films

T. J. PLUNKETT and J. K. A. CLARKE, *J. Catalysis*, 1974, **35**, (2), 330-334

X-ray diffractometry studies of the conversion of *n*-hexane and *n*-butane on Ir-Au films annealed in  $\text{H}_2$  for 1 h at 500°C showed peak doubling for 111 and 222 reflections for some alloy compositions, indicating two distinct regions of composition within the metal, while widths of deconvoluted individual peak components indicated homogeneity in such regions.

### Interaction between Iridium and Alumina in a Hydrazine Decomposition Catalyst

C. LECLERE, J. P. CONTOUR and G. PANNETIER, *Ann. Chim.*, 1974, **9**, (3), 221-230

Spectroscopic studies of the interaction between

Ir and  $\eta\text{-Al}_2\text{O}_3$  in a hydrazine decomposition catalyst showed that a part of chloroiridic acid is reduced during the impregnation of  $\text{Al}_2\text{O}_3$  giving a chlorinated complex of Ir(III) with structure undamaged by H at 400°C. The chemical shifts measured in photoelectron spectra confirm the presence of complexed Ir and show an electronic interaction between uncomplexed Ir and  $\text{Al}_2\text{O}_3$ .

### Activation of Nitrogen by Alkali Metal-promoted Transition Metal. III. On the Adsorption of Nitrogen over the Alkali Metal-promoted Ruthenium Catalyst

K.-I. AIKA and A. OZAKI, *J. Catalysis*, 1974, **35**, (1), 61-65

Studies of adsorption of  $\text{N}_2$  and  $\text{H}_2$  by alkali metal-promoted Ru on active C were made at 200-300°C and reduced pressures. Extensive  $\text{N}_2$  adsorption takes place on Ru-K and Ru-K/C, but not on Ru/C or K/C, which shows that  $\text{N}_2$  is first chemisorbed on Ru and migrates to alkali metal.

### Perovskites Containing Ruthenium as Catalysts for Nitric Oxide Reduction

R. J. H. VOORHOEVE, J. P. REMEIKA and L. E. TRIMBLE, *Mater. Res. Bull.*, 1974, **9**, (10), 1393-1404

Ru ions in the B sites of the perovskite-like ruthenates and manganites  $\text{ABO}_3$  (A is La, Pb, Sr, K and B is Ru or Mn + up to 10% Ru) are shown to be very active for NO reduction and losses of Ru by volatilisation are substantially reduced. Ruthenates and Ru ions diluted in  $\text{AMnO}_3$  have similar activity but the latter show lower  $\text{NH}_3$  production.

### Hydrogenation of Xylose over Platinum Group Catalysts

J. WISKIAK, M. HERSHKOWITZ and SHOSHANAH STEIN, *Ind. Engng. Chem., Prod. Res. Dev.*, 1974, **13**, (4), 232-236

Xylose was hydrogenated with Ru, Rh and Pd catalysts under a wide range of temperatures, pressure, catalyst concentration and agitation rates. The reaction is pseudo-first order and is controlled by the surface reaction between atomic H and unadsorbed Xylose. Kinetic surface parameters were determined for the Ru catalyst.

### The Dual State Behaviour of Supported Noble Metal Catalysts

K. C. TAYLOR, R. M. SINKEVITCH and R. L. KLIMISCH, *J. Catalysis*, 1974, **35**, (1), 34-43

The pretreatment dependent behaviour, which was able to generate two states differing in activity characteristics, was studied on the Ru catalyst, and selectivity changes were compared for Pt, Pd and Ru. S contamination measurements show that the effect is not a simple function of metal loading or dispersion. A mechanism involving surface reconstruction and/or metal-support interaction is proposed.

### Relationship between the Activity and the Excess Free Surface Energy of Noble Metal Catalysts

J. PETRÓ, É. POLYÁNSZKY and Z. CSÜRÖS, *J. Catalysis*, 1974, **35**, (2), 289-296

The relationship between the excess free surface energy ( $\Delta F$ ) of Pt, Pd, Ru and Ir catalysts and their catalytic hydrogenation activity was studied. The potential of the catalysts was measured in a 1 N HCl solution  $10^{-3}$  M with respect to its own ions, referred to the Ag/AgCl/HCl reference electrode. Results show a relationship between  $\Delta F$  and heat of sublimation.

## HOMOGENEOUS CATALYSIS

### Catalysis by Supported Transition Metal Complexes. IV. Hydrogenation of Acetylene Compounds on Palladium-containing Resin

M. PAEZ-PEDROZA, I. SCHIFTER and J.-E. GERMAIN, *Bull. Soc. Chim. Fr.*, 1974, (9-10, Pt. 2), 1977-1982

The activity per Pd atom of a catalyst prepared by ion-exchange of a basic resin is about twice that of Pd/C used in the hydrogenation of the triple bond of phenylacetylene or of 3-methyl-1-butyn-3-ol in alcohol solution. The allylic alcohol formed by semi-hydrogenation leads to a mixture of propanol and propanal. In this reaction, Pd/resin is eight times more active per Pd atom than Pd/charcoal.

### Catalytic Carboxylation of Fats: Carboxy Acids from Polyunsaturates

E. N. FRANKEL, F. L. THOMAS and W. F. KWOLEK, *J. Am. Oil Chem. Soc.*, 1974, **51**, (9), 393-396

Polyunsaturated fats were carboxylated in the presence of  $\text{PdCl}_2 \cdot \text{Ph}_3\text{P}$  with  $\text{H}_2\text{O}-\text{CO}$  at 120-160°C with or without acetone as a solvent. The highest yields of total carboxy and tricarboxy acids were achieved at low  $\text{Ph}_3\text{P}$  and  $\text{H}_2\text{O}$  levels, low temperatures, and high  $\text{PdCl}_2$  concentrations.

### Palladium-catalysed Amidation of Aryl, Heterocyclic, and Vinylic Halides

A. SCHOENBERG and R. F. HECK, *J. Org. Chem.*, 1974, **39**, (23), 3327-3331

Aryl, heterocyclic and vinylic halides react with CO and primary or secondary amines with a dihalobistriphenylphosphine Pd(II) catalyst at 100°C and 1 atm to form substituted amines. The reaction is highly stereospecific with *cis* and *trans* vinylic halides.

### Acetoxylation of Aromatic Compounds by Potassium Peroxydisulphate in Acetic Acid with Palladium(II) Complexes as Catalysts

L. EBERSON and L. JÖNSSON, *J. Chem. Soc., Chem. Commun.*, 1974, (21), 885-886

Aromatic compounds undergo a clean, predominantly *meta*-directing acetoxylation with potassium peroxydisulphate in glacial acetic acid, using  $\text{Pd}^{\text{II}}$  complexes with amines as catalysts.

### Palladium-catalysed Carboalkoxylation of Aryl, Benzyl and Vinylic Halides

A. SCHOENBERG, I. BARTOLETTI and R. F. HECK, *J. Org. Chem.*, 1974, **39**, (23), 3318-3326

Aryl and vinylic bromides and iodides, and benzyl chloride react with CO and an alcohol at 100°C and 1 atm in the presence of a tertiary amine and a catalytic amount of a Pd-triphenylphosphine complex to form esters. The reaction shows appreciable stereospecificity at 60-80°C with *cis* and *trans* vinylic halides producing esters with retained configuration.

### Complexes of Rhodium with Indigosulphonic Acids and Their Catalytic Properties

V. A. AVILOV, E. G. CHEPAIKIN and M. L. KHIDEKEL', *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1974, (11), 2559-2564

The binuclear complex of Rh with anion radicals of indigosulphonic acids is the active form for the catalytic hydrogenation of olefins. Heterogeneous catalysts of this type were produced for hydroformylation and carbonylation of olefins.

### Effect of Molecular Nitrogen on Coordination Metal Catalysis. I. Inhibiting Influence of Dinitrogen on the Isomerisation of 1-Pentene Catalysed by Dihydrido(dinitrogen) tris(triphenylphosphine)ruthenium

F. PENNELLA and R. L. BANKS, *J. Catalysis*, 1974, **35**, (1), 73-79

The isomerisation of 1-pentene is catalysed by  $\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3$  in toluene at 25°C. The kinetic data show that the catalytically active species are  $\text{RuH}_2(\text{PPh}_3)_3$  in the first isomerisation stage and  $\text{Ru}(\text{PPh}_3)_3$  in the second stage. The inhibiting effects of  $\text{N}_2$  are attributed to the ability of  $\text{N}_2$  to compete with the olefin for coordination to the metal.

### Homogenous Hydrogenation Using Osmium Complexes

A. OUDEMAN, F. VAN RANTWIJK and H. VAN BEKKUM, *J. Coord. Chem.*, 1974, **4**, (1), 1-7

$\text{Os}(\text{II})\text{ClH}(\text{PPh}_3)_3$  catalyst was studied during the hydrogenation of 1-alkenes and of some alkenes with activated double bonds. Stereoselective *cis* addition of H was demonstrated with suitable model compounds. In some cases the hydrogenation reaction was accompanied by *cis-trans* or positional isomerisation.

## CHEMICAL TECHNOLOGY

### Electrochemical and Corrosion Properties of Metal Ceramic Titanium-Palladium Alloy in Hydrochloric Acid Solutions

N. D. TOMASHOV, G. P. CHERNOVA and E. G. MANSKIT, *Zashchita Metal.*, 1974, **10**, (6), 643-647

Studies of the corrosion resistance of the metal

ceramic alloys 0.2, 0.4, 1.0 and 10% Pd-Ti made in 20% HCl electrolyte at 0.65 V showed that even the small addition of Pd (0.2-1.0%) in the alloys increased their corrosion resistance by one to two times from that of metal ceramic Ti. The best results were achieved on the metal ceramic alloy 10% Pd-Ti anodes in chlorine ion extraction.

## TEMPERATURE MEASUREMENT

### Balloon-borne Radiosonde for the Measurement of the Atmospheric Thermal Structure Coefficient

R. BARLETTI, P. LEMMETTI and L. PATERNO, *Mater. Sci. Engng.*, 1975, **18**, (1), 157-158

The characteristics and operational limits of a balloon-borne radiosonde with Pt wire temperature sensor working up to 20 km for the measurement of the atmospheric thermal structure coefficient  $C_T^{-2}$  are described.

## NEW PATENTS

### METALS AND ALLOYS

#### Contact Material

FUJITSU LTD. *U.S. Patent* 3,826,886  
A contact material having a high durability is prepared from an alloy consisting of 45-85 at.% Pd and 55-15 at.% Al.

#### Acoustic Devices Using Amorphous Metal Alloys

ALLIED CHEMICAL CORP. *U.S. Patent* 3,838,365  
Amorphous layers for use in acoustic alloys have a wide range of compositions but specifically include Pd<sub>77.5</sub>Ag<sub>6</sub>Si<sub>16.5</sub>, Pd<sub>76</sub>Cu<sub>5</sub>Si<sub>10</sub>, etc.

### ELECTRODEPOSITION AND SURFACE COATINGS

#### Electrically Conductive Composition Element

C.T.S. CORP. *U.S. Patent* 3,832,308  
An electrically conductive composition is mixed with a screening agent, deposited on a substrate and fired at an elevated temperature to form a terminal bonded to the substrate. The composition is a homogeneous mixture of approximately 70-95% co-precipitated Pt-Au alloy particles, co-precipitated Pd-Au alloy particles or co-precipitated Pt-Pd-Au particles and approximately 5-30% of glass frit.

### An Easily Calibrated, Versatile Platinum Resistance Thermometer

T. E. FOSTER, *Hewlett Packard J.*, 1974, **25**, (8), 13-17

Pt resistance wire with a wide range (-250 to +800°C) is used as the sensor for the new thermometer. Unusual features of this digital thermometer are a choice of normal or expanded resolution, linear analogue output, interchangeable probes, and many options including a battery pack and digital output.

### Stabilisation of Metal-sheathed Thermocouples

J. E. BARD, *Instrum. Technol.*, 1974, **21**, (10), 50-51  
Microanalytical measurements of a 10% Rh-Pt sheathed, magnesia-insulated Pt:13% Rh-Pt thermocouple at a steady 1450°C showed them to drift more than 200°C after 1400 h. Rh from both the sheath and the positive thermoelement (13% Rh-Pt) had migrated to the negative thermoelement (Pt), and this occurred at locations well removed from the hot junction.

### LABORATORY APPARATUS AND TECHNIQUE

#### Alloy Tension Band

FA. CARL HAAS *British Patent* 1,378,835  
Tension bonds for measuring instruments are made from alloys containing at least 50% Pd and/or Pt and less than 50% of at least one Group III to VI element (excluding B, C, N, O and the transition elements), e.g. Al, Sb, Te, Sn, Ca. About 1-30% Au, Ag or Cu may also be present. A typical alloy contains 4% Al, 4% Ag, and Pd.

### HETEROGENEOUS CATALYSIS

#### Exhaust Catalyst

W. R. GRACE & CO. *British Patent* 1,374,064  
Pd and/or Pt on ceramic monolithic catalyst is improved by the presence of a number of linear and parallel passages for gas flow.

#### Hydrocarbon Isomerisation Catalyst

UNIVERSAL OIL PRODUCTS CO. *British Patent* 1,374,863  
Saturated and unsaturated hydrocarbons may be isomerised over a catalyst containing Pt or another Pt metal, a halide, a reaction product of a Friedel-Crafts metal halide and the Al<sub>2</sub>O<sub>3</sub> support, and either a Re component or a germanium component in an oxidation state greater than elementary metal.