

# ABSTRACTS

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

### PROPERTIES

#### **Contribution to the Short-time Creep Strength of Platinum Materials. VII. Pt-Pd-Rh Alloys at 1400°C**

G. REINACHER, *Metall.*, 1971, 25, (7), 740-748

In the search for a material comparable to 90% Pt-Rh with regard to heat and corrosion resistance the behaviour of six Pt-Pd-Rh alloys with 40-70% Pd was studied at 1000-1400°C. The alloy 50%Pt-40%Pd-10%Rh was found to be the best with regard to these properties to replace the standard alloy.

#### **Investigation of the Reaction of Hydrogen with Some Pd-Au and Pd-Ag-Au Alloys**

A. A. RODINA, M. A. GUREVICH and N. I. DORONICHEVA, *Zh. Fiz. Khim.*, 1971, 45, (5), 1110-1113

The permeability of Pd-Au and Pd-Ag-Au alloys for H<sub>2</sub> and their stability in H<sub>2</sub> for repeated changes of temperature was investigated. The permeability of ternary Pd-Ag-Au exceeds that of pure Pd, but the permeability of binary Pd-Au alloys is close to that of Pd. The alloys are more stable in H<sub>2</sub> than in pure Pd, but their stability is less than Pd-Ni and Pd-Ag-Ni alloys.

#### **Temperature-dependent Scattering in Paramagnetic PdCo Alloys**

J. W. LORAM, G. WILLIAMS and G. A. SWALLOW, *Phys. Rev. B: Solid State*, 1971, 3, (9), 3060-3065

The resistivities of dilute PdCo alloys at temperatures above the magnetic ordering temperature were measured. The excess resistivity  $\Delta\rho = A + B \ln T$  (where B is positive) and is proportional to Co concentration.

#### **Magneto-resistance Measurements on Ferromagnetic PdFe and PdCo Alloys**

*Ibid.*, (11), 3863-3873

The temperature dependence of the resistivity of 0.78 at.% Fe-Pd and 0.73 at.% Co-Pd was measured at 1.4-20K and up to 60kOe. Results are discussed in terms of a model based on s-electron scattering from collective excitations in the coupled impurity moment d-band system of the alloy.

#### **Effect of Thermal Treatment and Plastic Deformation on the Magnetic Properties of Iron-Palladium-Cobalt Alloys**

V. I. ZEL'DOVICH, I. G. AZARKOVA and V. M. SCHASTLIVTSEV, *Fiz. Metal. Metalloved.*, 1971, 31, (6), 1198-1206

The coercivity of Fe-Pd alloys after annealing can

be increased by preliminary plastic deformation and by reducing the annealing temperature. Co introduced into 33 and 35 at.% Pd-Fe increases the magnetisation and residual magnetism under optimum conditions. X-ray studies and data on coercivity, annealing time and Pd content suggest that phase conversions of ordering  $\gamma_0 \rightarrow \gamma_1$  and of decomposition  $\gamma_0 \rightarrow \gamma_1 + \alpha$  are mainly of one kind.

#### **The Structure of Nickel-Palladium Solid Solutions**

W. LIN and J. E. SPRUIELL, *Acta Metall.*, 1971, 19, (5), 451-461

Local atomic arrangements and atomic displacements from their average positions were investigated for 25, 50 and 75 at.% Pd-Ni using a single crystal X-ray diffuse scattering technique. Ni-Pd alloys have short wavelength composition modulations along (100) directions when slowly cooled from high temperatures or heat treated at relatively low temperatures following quenching. A computer simulation was used to generate a model of the local atomic arrangements in the slowly cooled 50 at.% Pd-Ni alloy.

#### **Thermo-e.m.f. of Solid Solutions of the Pd-Ni-Cu System**

G. I. TEREKHOV, S. I. SINYAKOVA and O. S. IVANOV, *Izv. Akad. Nauk S.S.S.R., Metall.*, 1971, (3), 201-205

Studies of the thermo-e.m.f. of solid solutions of Pd-Ni-Cu formed from Ni-Cu and Pd-Cu alloys showed that the thermo-e.m.f. decreases almost directly as Pd concentration increases.

#### **Thermodynamic Properties and Ordering in PdAl**

M. ETTENBERG, K. L. KOMAREK and E. MILLER, *Metall. Trans.*, 1971, 2, (4), 1173-1181

The activity of Al in the Pd-Al system was determined by an isopiestic method in 30-80 at.% Al-Pd at 1090-1490K. It showed a strong negative deviation from ideality with a decrease in Al activity of four orders of magnitude around the stoichiometric composition PdAl. The defect structure in the CsCl-type PdAl compound was found by lattice parameter measurements.

#### **The Mechanical Properties of Palladium 20 at% Silicon Alloy Quenched from the Liquid State**

T. MASUMOTO and R. MADDIN, *Acta Metall.*, 1971, 19, (7), 725-741

The elastic and plastic properties of filaments of

non-crystalline 20 at. % Si-Pd and the changes that occur on crystallisation during and after heating were examined. The non-crystalline structure was stable below 275°C but transformed on heating at or above 300°C to a f.c.c. structure, then to an unknown structure and finally to the stable orthorhombic Pd<sub>3</sub>Si.

#### The Rhodium/Copper Constitution Diagram

C. RAUB, E. RÖSCHEL, D. MENZEL and M. GADHOF, *Metall*, 1971, 25, (7), 761-762

The Rh-Cu system was studied from 600-2200°C. The system has marked similarities to the Au-Pt system, but not to the Ag-Pt. At ~1200°C Rh and Cu are completely miscible in the solid state. For 60 at. % Ru-Cu the critical immiscibility temperature is 1150°C.

#### Superconductivity of Re-Os, Re-Ru, Ru-Os, and Re-W H.C.P. Alloy Systems

C. W. CHU and W. L. MCMILLAN, *Phys. Rev. B: Solid State*, 1971, 3, (11), 3757-3762

The superconductivity transition temperature  $T_c$  was measured for the h.c.p. Re-Os, Re-Ru, Ru-Os, and Re-W systems and for slightly doped Re. A sharp peak in the graph of  $T_c$  vs. Os-concentration is attributed to the Fermi surface topology change in Re due to alloying. A small addition of impurities invariably increases the  $T_c$  of Re due to band-structure smearing and the Fermi surface topology change.

## CHEMICAL COMPOUNDS

#### A Neutron Diffraction Study of Palladium Hydride

G. NELIN, *Phys. Status Solidi*, 1971, 45, (2), 527-536

Neutron diffraction measurements were made on PdH<sub>x</sub> formed by soaking powdered Pd in H<sub>2</sub>. Results show that H occupies octahedral interstices in both the  $\alpha$  and  $\beta$  hydrides.

#### Geometrical Isomers of $\pi$ -Allyl Complexes of Palladium Chloride and Dienes

O. G. LEVANDA, G. YU. PEK and I. I. MOISEEV, *Zh. Org. Khim.*, 1971, 7, (2), 217-223

Conjugated dienes react with PdCl<sub>2</sub> in CH<sub>3</sub>COOH to form  $\pi$ -allyl complexes containing CH<sub>2</sub>OAc groups, which mainly occupy *syn*-positions for butadiene and isoprene complexes but *anti*-positions for 2,3-dimethylbutadiene complexes. During the decomposition of butadiene-acetic acid complexes, diacetates of erythrol and of *cis*- and *trans*-butene-2-diol-1,4 are formed in the ratio 2:1:7.

#### Crystal Growth and Semiconductivity of Palladium Oxide

D. B. ROGERS, R. D. SHANNON and J. L. GILLSON, *J. Solid State Chem.*, 1971, 3, (2), 314-316

A method of growing crystals of PdO by vapour

transport is described. Electrical measurements of the product crystals show semiconductivity with a low activation energy that is probably extrinsic. A bonding model consistent with semiconductivity in PdO is proposed.

#### Tertiary Phosphine-Palladium(0)-Ethylene Complexes

R. VAN DER LINDE and R. O. DE JONGH, *J. Chem. Soc., D, Chem. Commun.*, 1971, (11), 563

The synthesis of L<sub>2</sub>Pd-ethylene complexes (L = PPh<sub>3</sub>, tricyclohexylphosphine or tri-*o*-tolylphosphite) and of L<sub>2</sub>Pd (L = tricyclohexylphosphine) is reported. These may serve as starting materials in oxidative addition reactions.

#### Thermodynamic Properties of RuO<sub>2</sub>

D. CHATTERJI and R. W. VEST, *J. Am. Ceram. Soc.*, 1971, 54, (2), 73-74

The free energy change for the reaction RuO<sub>2</sub>(s) + 4Cu(s) = 2Cu<sub>2</sub>O(s) + Ru(s) was measured at 600-1000°C from e.m.f. measurements on a solid galvanic cell using a stabilised ZrO<sub>2</sub> electrolyte. The standard molar free energy of formation of RuO<sub>2</sub> is  $\Delta G^\circ_{\text{RuO}_2} = -71,400 + 38.97T \pm 120$  cal/mol. The standard molar enthalpy and entropy of formation of RuO<sub>2</sub> at 298K are  $-72,430 \pm 200$  cal/mol and  $-40.44 \pm 0.2$  e.u. respectively. Its absolute entropy at 298K is  $15.46 \pm 0.2$  e.u.

## ELECTROCHEMISTRY

#### Sorption of Oxygen from Solution by Noble Metals. I. Bright Platinum

R. THACKER and J. P. HOARE, *J. Electroanal. Chem. Interfac. Electrochem.*, 1971, 30, (1), 1-13

Pt bead or wire electrodes adsorbed O<sub>2</sub> from O<sub>2</sub>-saturated H<sub>2</sub>SO<sub>4</sub> under steady state conditions. Two kinds of adsorption sites were identified, strong ones in the skin of the metal and weak ones on the metal surface. A complete layer of Pt-O was obtained by anodising at  $\approx 1600$  mV. At > 2000 mV PtO<sub>2</sub> is formed.

#### II. Nitric Acid-passivated Bright Platinum

J. P. HOARE, R. THACKER and C. R. WIESE, *Ibid.*, 15-22

The nature of the adsorbed films on Pt electrodes treated with concentrated HNO<sub>3</sub> was studied. The dissolved O<sub>2</sub> of the Pt-O alloy does not come from the HNO<sub>3</sub>; the acid serves to make the Pt more accommodating to sorption of O<sub>2</sub>.

#### Electrochemical Polarisation of Physiological Electrodes: Platinum Anodes in Sulphate, Chloride and Sulphate-Chloride Solutions

B. J. PIERSMA, F. SHANNON, S. CALHOON and W. GREATBATCH, *Extended Abstr., 139th Natl. Mtg., Electrochem. Soc.*, 1971, (May), 347-348, abstr. 143

The behaviour of Pt-bead electrodes in sulphate, chloride and sulphate-chloride solutions was studied by applying anodic pulses from open circuit potentials controlled by saturating the

solution with  $H_2$ . The charge required to remove adsorbed H atoms was constant and independent of  $Cl^-$  concentration.

#### **Decomposition of Hydrogen Peroxide on Platinum and Methods for its Study**

A. A. REIKHARDT, *Zh. Fiz. Khim.*, 1971, **45**, (5) 1220-1222

The relation of the heat of catalytic decomposition of  $H_2O_2$  in dynamic conditions on Pt black to the concentration of solution is discussed. During polarisation of the Pt by a.c. the activity of the catalyst increased and the reproducibility of the results increased.

#### **The Electrochemical Oxidation of 1-Pentyne on Platinum and Gold**

M. J. DANIELSON, *Diss. Abstr. B*, 1971, **31**, (11), 6531

The anodic oxidation of 1-pentyne was studied at 70°C on Pt and Au electrodes in solutions of  $H_2SO_4$ ,  $K_2SO_4$ ,  $K_2CO_3$  and KOH at pH 0.35-12.7 for Pt, and pH 10.9-12.7 for Au. Reaction rates were measured as a function of potential, pH, temperature and 1-pentyne partial pressure.

#### **Reaction of Mercury with the Surface of Platinum- and Osmium-coated Platinum Electrodes during Poisoning by Mercuric Chloride**

A. A. SUTYAGINA, V. I. FADEEVA, I. N. GOLYANITSKAYA and G. D. VOCHENKO, *Zh. Fiz. Khim.*, 1971, **45**, (7), 1782-1783

Calomel or atomic Hg is formed on the surfaces of Pt/Pt and Os/Pt electrodes by mercuric chloride poisoning.  $\beta$ -PtHg<sub>4</sub> is formed on Pt/Pt but not on Os/Pt.

#### **The Surface Composition of Platinum-Gold Alloys**

R. WOODS, *Electrochim. Acta*, 1971, **16**, (5), 655-659

Homogeneous alloys were prepared by melting a weighed quantity of Au on to a Pt wire in glass and then melting the metals together. Electrochemical measurements on the alloys were taken at 25°C in 1 M  $H_2SO_4$ . The alloy electrodes gave current/potential curves equivalent to the sum of a pure Pt and pure Au surface. This indicates that the Pt-Au alloys separate at the surface into the equilibrium  $\alpha_1$  and  $\alpha_2$  phases irrespective of bulk composition.

#### **Investigation of the Self-passivation Processes of Ti-Pd Alloys and the Accumulation of Palladium on their Surfaces during Corrosion in Sulphuric Acid Solutions**

N. D. TOMASHOV, T. V. CHUKALOVSKAYA and G. P. CHERNOVA, *Zashchita Metal.*, 1971, **7**, (3), 279-283  
0.2% and 0.86% Pd-Ti alloys in 40%  $H_2SO_4$  at 100°C become passive as Pd accumulates on their

surfaces. Studies of this process during corrosion showed that the concentration of Pd at the surface rises with time and is greater with the 0.86% Pd alloy. The Pd accumulates at the alloy surface in the form of finely dispersed crystals.

#### **The Nature of Adsorbed Oxygen on Rhodium, Palladium and Gold Electrodes**

D. A. RAND and R. WOODS, *J. Electroanal. Chem. Interfac. Electrochem.*, 1971, **31**, (1), 29-38

O coverage was determined on Rh, Pd and Au anodes as a function of potential and time. The O-containing film consists of chemisorbed O atoms, but phase oxide can nucleate and grow under severe anodising conditions. A basis for distinguishing between the two is presented.

#### **Investigation of the Kinetics of Reduction of Allyl Alcohol and of Butyraldehyde on Osmium Catalyst by Electrochemical Methods**

I. V. KUDRYASHOV, I. A. MAKOLKIN and N. N. NIKOLAEV, *Zh. Fiz. Khim.*, 1971, **45**, (7), 1694-1697

The effect of temperature was recorded automatically during hydrogenations of butyraldehyde and allyl alcohol on an Os electrode. Order of the reactions and activation energies were determined. A new method for coating electrodes with Os is proposed. Os has high catalytic activity for hydration of double bonds and of carbonyl groups.

#### **Study of the Kinetics of the Reduction of Maleic Acid on Rhodium Catalyst**

I. V. KUDRYASHOV, A. V. IZMAILOV and D. G. NARYSHKIN, *Ibid.*, (6), 1458-1461

Electrochemical studies of kinetics of maleic acid hydrogenation by  $H_2$  on Rh black enabled the rate constants and effective activation energy to be calculated.

## **ELECTRODEPOSITION AND SURFACE COATINGS**

#### **Electrodeposition of Platinum from Chloride Solutions Containing Chloroplatinate and Chloroplatinite**

I. B. OBUKHOVA and B. S. KRASIKOV, *Zh. Prikladnoi Khim.*, 1971, **44**, (5), 1025-1033

The kinetics were established for the two-stage reduction of chloroplatinate to chloroplatinite and thence to Pt, using various chloroplatinate solutions at pH 0-1.5, Pt concentration 0.025 mole/l, 20-40°C, 0.9-3.3 g-ion/l  $Cl^-$ . A fast partial aquation of chloro-complexes of Pt is involved. Reduction of chloroplatinite to Pt at potentials  $\leq 0.1$  V occurs with partial adsorption by Pt of  $H_2$  limited by the current for which reduction of chloroplatinate to chloroplatinite occurs.

### Study of Electrodeposition of Palladium-Silver Alloys from Nitrate Electrolyte

A. YA. PRONSKAYA, S. I. KRICHMAR and S. D. OKHRIMETS, *Elektrokhimiya*, 1971, 7, (6), 778-781  
Studies of the effects of temperature, pH, current density, and nitrate solution strength during the electrodeposition of Pd-Ag alloys enabled optimum conditions to be established.

### Rhodium and Palladium Plating in the Jewellery Industry

A. PIANELLI, *Galvano*, 1971, 40, (412), 599-602  
The relative merits of electrodeposited Pd and Rh on jewellery and spectacles is discussed, and methods of plating are described. Rh is preferred to Pd because it gives a whiter deposit with greater hardness and resistance, and because the Rh electrolytes are easier to produce and use.

## HETEROGENEOUS CATALYSIS

### Catalytic Reforming

M. J. STERBA and V. HAENSEL, *World Petroleum*, 1971, 42, (5), 192-202

A history of the development of catalytic reforming is given. The improved selectivity and activity of newer Pt-Re catalysts under severe operating conditions has allowed the use of lower pressures during reforming reactions, which gives better catalyst life and higher yields of motor fuel reformat, aromatics and H<sub>2</sub>.

### Manufacturing Tomorrow's Gasolines.

#### Parts 1 and 2

L. O. STINE, R. M. DEVEIRMAN and R. P. SCHULLER, *Oil Gas J.*, 1971, 69, (22, May 31), 49-53; *Ibid.*, (23, June 7), 76-82

The changes in the content of petrol required to meet the U.S. anti-pollution laws are outlined. The use of platforming catalysts, particularly Pt-Re, in improving octane quality is discussed.

### UOP Unveils Advanced New Platformer

*Ibid.*, (20, May 17), 84-85

A 20,000 b/sd unit platformer, on stream at Coastal States Petrochemical Company's Corpus Christi plant, can operate as a fixed bed, semi-regenerative or continuous regenerative unit. It uses an R-16-type catalyst, which contains Pt and Re, and employs low-pressure operation. UOP claim higher reformat and H<sub>2</sub> yields and longer on-stream time for their catalyst.

### Petroleum-refinery Catalytic Reforming

*Chem. Engng.*, 1971, 78, (12, May 31), 18-19

At the American Petroleum Institute's Division of Refining Meeting in San Francisco in May UOP announced a new version of their platforming process which combines low-pressure operation with a continuous catalyst regeneration system. This uses the R-16 Pt-Re catalyst. Esso

Research and Engineering reported on studies on developing cyclic Powerforming flow sheet where-in reactors containing a Pt catalyst are cyclically and frequently regenerated. The reformers give improved yield with good catalyst activity and selectivity.

### Isomerisation Is in as Lead Additives Go out

N. P. CHOPEY, *Ibid.*, 24-26

Different catalyst systems for isomerisation are compared. British Petroleum use fixed-bed noble metal catalyst for their low temperature (250-350°F) and low pressure (250-400 lb/in<sup>2</sup>/gauge) process. Shell use a strongly acidic zeolite with a highly dispersed noble metal. Vapour phase isomerisation takes place at 150-350 lb/in<sup>2</sup>, and 400-550°F.

### Characteristics of Pt-Rh Gauze Catalyst and Kinetics of the HCN Synthesis

B. Y. K. PAN, *J. Catalysis*, 1971, 21, (1), 27-38

Investigations were carried out of HCN synthesis by combustion of CH<sub>4</sub>, air and NH<sub>3</sub> over Pt-Rh gauze catalyst. A new catalyst after 60-80h activation maintained its economical life for several thousand hours. Conditions for maximum conversion NH<sub>3</sub> to HCN were found; at this stage the rate of HCN formation was  $\approx$  first order with respect to NH<sub>3</sub> and CH<sub>4</sub>.

### Catalytic Synthesis of Ammonia in Barrier Discharges

E. N. EREMIN, A. N. MAL'TSEV and V. L. SYADUK, *Zh. Fiz. Khim.*, 1971, 45, (5), 1135-1139

The activity of metallic catalysts for NH<sub>3</sub> synthesis from N<sub>2</sub>-H<sub>2</sub> mixtures was Pd > Pt > Fe > Cu > Ni. Palladised Pd and platinised Pt with highly developed surface areas are the most active. A heterogeneous-ion mechanism for the synthesis of NH<sub>3</sub> in barrier discharges is proposed.

### Catalytic Oxidation Studies with Platinum and Palladium

A. SCHWARTZ, L. L. HOLBROOK and H. WISE, *J. Catalysis*, 1971, 21, (2), 199-207

The relationship between the chemical structure of reactants, alkanes, alkenes, alcohols and ketones, oxidised on Pt and Pd filaments, and the activation entropy and energy was studied. Fractional surface coverage of the catalyst with chemisorbed O and H abstraction from the organic compound appears to control the rates of catalytic oxidation. Pd is less efficient than Pt due to the formation of PdO which exhibits properties of a metal-oxide semiconductor.

### On the Effect of the Method of Preparation on the Catalytic Activity of Platinum Black

A. P. GOROKHOV, A. B. FASMAN and D. V. SOKOL'SKII, *Kinet. Kataliz*, 1971, 12, (3), 690-693

Parameters affecting the catalytic activity of Pt black were studied during its preparation. The

greatest modifying influences are the state of the internal coordination in Pt(IV) acido complexes, the nature and concentration of added modifying ions, and the liquid phase during reduction of  $\text{PtO}_2$ . The added ions modify the catalyst by inhibiting growth of crystals and grains of  $\text{PtO}_2$  and Pt black.

### Energetic Activation of Heterogeneous Catalysts

A. N. MAL'TSEV, N. I. KOBOZEV and L. V. VORONOVA, *Zh. Fiz. Khim.*, 1971, **45**, (7), 1719-1722

During the hydrogenation of acrylic acid on Pt and Rh blacks small amounts of  $\text{H}_2\text{O}_2$  were added and were reduced to  $\text{H}_2\text{O}$  with the liberation of  $\sim 92$  kcal/mole. This leads to the formation of new centres of hydrogenation on the blacks. When reducing 1 mole  $\text{H}_2\text{O}_2$  at 1 g.atom/min the rate of hydrogenation of acrylic acid rises from 1.5 to 4 mole/g.atom/min.

### The Mechanism of Sintering of Platinum Catalysts in Atmospheric Air

S. A. KHAASSAN, L. F. ATYAKSHEVA and G. I. EMEL'YANOVA, *Ibid.*, (6), 1517-1520

Studies of the sintering of Pt black and adsorbed  $\text{Pt}/\text{Al}_2\text{O}_3$  in air show that there is a steady decline in activity and in surface area related to the duration and temperature of roasting. Sintering of adsorbed catalysts is accompanied by a great change in the volume. Results are compared with those for vacuum sintering.

### Coke Formation during the Aromatisation of *N*-Paraffins in the Presence of Platinum/Alumina Catalysts

T. V. KURCHATKINA, YU. V. FOMICHEV and M. E. LEVINTER, *Neftekhimiya*, 1971, **11**, (3), 371-375

The yields of coke during aromatisation over AP-64  $\text{Pt}/\text{Al}_2\text{O}_3$  catalyst at 1 atm in a stream of  $\text{H}_2$  is higher from  $N\text{-C}_6\text{H}_{14}$  than from  $N\text{-C}_7\text{H}_{16}$  or  $N\text{-C}_8\text{H}_{18}$ . Under these conditions alkylcyclopentanes produced during  $\text{C}_5$ -dehydrocyclisation of *N*-paraffins take part in the coke formation. The tendency to form coke depends on the structure of the alkylcyclopentane, which is related to the initial paraffin. Coke yields during aromatisation of  $N\text{-C}_6\text{H}_{20}$  and  $N\text{-C}_{10}\text{H}_{22}$  are greater than from  $N\text{-C}_6\text{H}_{14}$ ,  $N\text{-C}_7\text{H}_{16}$  and  $N\text{-C}_8\text{H}_{18}$ .

### Hydrogen Chloride Activation of Alumina and Platinum/Alumina

J. W. MYERS, *Ind. Engng. Chem., Product Res. Dev.*, 1971, **10**, (2), 200-203

Activation of  $\text{Pt}/\text{Al}_2\text{O}_3$  with anhydrous HCl at 480-760°C gave very active catalysts that isomerised  $\text{C}_4\text{H}_{10}$  at 65°C. Activity was a maximum after activation at 650°C. Pt participates directly in the isomerisation.  $\text{H}_2$  pretreatment before activation increases the activity by minimising the adsorption of poisons during chloriding.

### On the Effect on the Activity of Platinum/Alumina Catalysts of the Method of Depositing the Platinum

G. N. MASLYANSKII, B. B. ZHARKOV and A. Z. RUBINOV, *Kinet. Kataliz*, 1971, **12**, (3), 784-785

Additions of  $\text{CH}_3\text{COOH}$  and  $\text{HNO}_3$  to aqueous  $\text{H}_2\text{PtCl}_6$  solutions during impregnation of active  $\text{Al}_2\text{O}_3$  significantly increase the activity of  $\text{Pt}/\text{Al}_2\text{O}_3$  catalysts for hydrogenations of  $\text{C}_6\text{H}_6$  and cyclohexene. Activity for hydrogenation depends on the concentration of acid added; optimum amounts are 5-10% of  $\text{CH}_3\text{COOH}$  and 1-2% of  $\text{HNO}_3$ .

### Reaction Paths for Decyclisation of Methylcyclopentane over $\text{Pt}/\text{Al}_2\text{O}_3$ Catalyst

R. L. SMITH, P. A. NARO and A. J. SILVESTRI, *J. Catalysis*, 1971, **20**, (3), 359-366

Using poisoning techniques and mixed catalysts, the decyclisation of methylcyclopentane on duofunctional  $\text{Pt}/\text{Al}_2\text{O}_3$  was studied. The reaction was shown to proceed by an acid-dependent route as well as by an acid-independent Pt catalysed mechanism.

### $\text{O}_2$ Chemisorption at High Temperatures on Platinum-Alumina and Platinum-Zeolite

S. W. WELLER and A. A. MONTAGNA, *Ibid.*, 394-407

The adsorption and desorption of  $\text{O}_2$  on  $\text{Pt}/\text{Al}_2\text{O}_3$  and  $\text{Pt}/\text{Zeolite Y}$  was studied at 475 and 525°C.  $\text{H}_2$  chemisorption at 200°C was used as a measure of Pt dispersion. For  $\text{Pt}/\text{Zeolite Y}$  the limiting O:Pt atom ratio was  $\approx 0.86:1$ ; for  $\text{Pt}/\text{Al}_2\text{O}_3$  it was 3.7:1 at 525°C. The limiting ratio H:total Pt is 1:1 for  $\text{Pt}/\text{Al}_2\text{O}_3$  but 2:1 for  $\text{Pt}/\text{Zeolite Y}$ . The latter was the more susceptible to sintering.

### Regularity of Change of Catalytic and Structural Properties of the Surface of Adsorption $\text{Pt}/\text{SiO}_2$ Catalysts

N. I. KOBOZEV, G. I. EMEL'YANOVA and S. G. FEDORKINA, *Zh. Fiz. Khim.*, 1971, **45**, (5), 1213-1216

The influence of temperature on the catalytic and structural properties of  $\text{Pt}/\text{SiO}_2$  adsorption catalysts was studied. Heating at 400-600°C produces greater activation and increases in the active surface.

### Investigation of the Efficiency of $\text{Pt}/\text{Zeolite}$ Catalysts in the Decomposition of $\text{H}_2\text{O}_2$ .

#### I. Activity of $\text{Pt}/\text{Zeolite}$ Catalysts Produced by the Method of Impregnation

T. A. POSPELOVA, V. I. SHEKHOBALOVA, N. I. KOBOZEV and T. L. METT, *Ibid.*, (6), 1462-1466

Isothermal studies of the efficiency of  $\text{Pt}/\text{NaY}$  zeolite catalyst ( $\text{SiO}_2/\text{Al}_2\text{O}_3=4.8$ ) for decomposition of 0.2 to 16N solutions of  $\text{H}_2\text{O}_2$ , where zeolite alone is inactive, show increased efficiencies for small (0.4%) and large (4-6%) Pt concentrations. These increases are due to the

activity of individual Pt atoms and to possible recuperative effects for large Pt contents at high  $H_2O_2$  solution concentrations. Activation energy is 13.6 kcal/mole.

## II. Efficiency of Pt/Zelite Catalysts Produced by the Method of Implantation

*Ibid.*, (7), 1715-1718

The activity and efficiency of Pt/NaY zeolite, in which  $SiO_2/Al_2O_3=4.8$  and 4.3, were determined isothermally for  $H_2O_2$  decomposition. Two types exist with activities differing by  $\sim 3$  times. Catalysts produced by implantation and impregnation were compared. Activity is affected by the capacity of the catalysts to accept the metals. Activation energy is not related to the method of using the catalyst and amounts to 13.7 kcal/mole.

## The Effect of Sulphur and Nitrogen Compounds on the Properties of Platinum and Palladium Catalysts on Alumina and Zeolites

N. R. BURSIA, YU. A. SHAVANDIN, G. V. STAVROVA and N. K. VOLNUKHINA, *Kinet. Kataliz*, 1971, 12, (3), 769-772

The action of S- and N-compound catalyst poisons and the effect of the catalyst support was studied on Pt and Pd catalysts supported on both  $Al_2O_3$  and CaY faujasite zeolites.

## Dehydrocyclisation of N-Hexane in the Presence of Palladium/Alumina Catalysts in a Stream of Helium and Hydrogen

V. S. FADEEV, I. V. GOSTUNSKAYA and B. A. KAZANSKII, *Neftekhimiya*, 1971, 11, (3), 366-370

Studies of  $N-C_6H_{14}$  conversion over Pd/ $Al_2O_3$  in relation to temperature, contact time and carrier gas show that the yield of  $C_6H_6$  is higher in He than in  $H_2$  at all ranges of temperature. Thus, aromatisation of  $N-C_6H_{14}$  over Pd/ $Al_2O_3$  leads to the formation of unsaturated hydrocarbons as intermediate reaction products.

## Deuteration, Isomerisation and Exchange of Cyclo-olefins over Palladium Catalysts

L. HILAIRE and F. G. GAULT, *J. Catalysis*, 1971, 20, (3), 267-287

The deuteration, exchange and isomerisation of cyclopentenes and other 4-5 ring cyclo-olefins was studied over Pd films and Pd/pumice. The *cis:trans* distribution depended mostly on the size of the ring. The results show that deuteration does not proceed by the same mechanism as the double bond migration and the olefin exchange.

## Effect of Several Factors on Liquid Phase Oxidation of Ethylene with Palladium Chloride-Active Charcoal Catalyst

K. FUJIMOTO, O. KUCHIISHI and T. KUNIGI, *Kogyo Kagaku Zasshi*, 1971, 74, (2), 179-182

Liquid phase oxidation of  $C_2H_4$  with PdCl<sub>2</sub>/C

was studied with respect to factors affecting  $C_2H_2$  yield. The reaction was suppressed by HCl. The overall activation energy was  $\approx 10$  kcal/mol. Maximum selectivity was obtained at 80-90°C. The maximum reaction rate occurred when the molar ratio of  $C_2H_4$  to  $O_2$  was 4:1.

## Catalysis by Supported Transition Metals Complexes. I. Palladium Chloride on Ion Exchange Resin

R. LINARTE LAZCANO and J. E. GERMAIN, *Bull. Soc. Chim. Fr.*, 1971, (5), 1869-1874

The ion exchange between a basic resin and an aqueous solution of Pd(II)Cl<sub>4</sub><sup>2-</sup> gives a solid able to catalyse the hydrogenation of olefins in alcoholic solution at 25°C and 1 atm. The kinetics indicate active centres different to those of metallic Pd.

## Metallopolymers on the Basis of Highly Dispersed Palladium Epoxy Resins and Polyvinyl Acetates as Catalysts for Hydrogenation of Organic Compounds

V. M. VARUSHCHENKO, S. A. MIKHALYUK, E. M. NATANSON and B. D. POLKOVNIKOV, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1971, (6), 1346-1349

These Pd/polymer catalysts have a high activity for hydrogenation of various organic compounds and retain this during long storage exposed to air.

## Structure and Physico-chemical Properties of Palladium-Rhodium Catalysts

A. M. SOKOL'SKAYA, S. A. RYABININA, A. P. GOROKHOV and YU. F. KLYUCHNIKOV, *Kinet. Kataliz*, 1971, 12, (3), 706-711

The catalytic and electrochemical properties and structure of Pd-Rh catalysts were studied. High dispersion of Rh black increases the specific surface of the mixed catalyst. The mixed catalysts are significantly more active than pure Pd and Rh for hydrogenation of some organic compounds. The electrochemical activity of the Pd-Rh catalyst rises as the Rh content increases.

## The Hydrogenation of Aniline over Supported Rhodium-Palladium Alloy Catalysts

K. IKEDATE and S. SUZUKI, *Bull. Chem. Soc. Japan*, 1971, 44, (2), 325-330

The hydrogenation of aniline was investigated at 30-50°C over Rh-Pd/C. Activity was a maximum at 75-85 wt.% Rh, but activity/unit surface area was at 25 wt.% Rh, coinciding with the minimum in activation energy. Maximum selectivity was observed at 20-30 wt.% Rh.

## Catalytic Dehydrogenation of Coal: Part 6. Yield of Hydrogen from Whole Coal

L. REGGEL, I. WENDER and R. RAYMOND, *Fuel*, 1971, 50, (2), 152-156

The use of supported Pd catalysts is described in the dehydrogenation of whole coal. Results are compared with those for the dehydrogenation of

vitrimines from bituminous coals, and it is found that the yield of H<sub>2</sub> gas is only slightly lower for the whole coal. Whole coal would be suitable in a commercial process for catalytic hydrogenation without separation of macerals.

### Stability of a Porous Catalyst Subjected to Carbon Deposition

J. G. FIRTH and H. B. HOLLAND, *J. Appl. Chem. Biotechnol.*, 1971, 21, (5), 139-140

A study was made of the stability of porous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>-based Pt metal catalysts subjected to C deposition during the catalytic oxidation of CH<sub>4</sub>. The stability was found to be directly proportional to the mechanical strength of the Al<sub>2</sub>O<sub>3</sub>.

### Activity of Metal Catalysts. I. Hydrogenolysis of Cyclopentane on Group VIII Metals

R. MAUREL and G. LECLERCQ, *Bull. Soc. Chim. Fr.*, 1971, (4), 1234-1239

Hydrogenolysis of cyclopentane was studied at 120-330°C over Group VIII metals on Al<sub>2</sub>O<sub>3</sub>. Pt and Pd gave only *N*-C<sub>5</sub>H<sub>12</sub>; Ru, Rh, Os, Ir, Co and Ni gave also CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub> and C<sub>4</sub>H<sub>10</sub>. The Arrhenius curve was plotted for each metal. In order of increasing activity at 182°C they are Cu, Fe, Pd, Pt, Ni, Co, Os, Rh  $\approx$  Ir, Ru.

### II. Epimerisation of *cis*-1,2-Dimethylcyclohexane on Group VIII Metals

R. MAUREL, G. LECLERCQ, P. HELL and L. LECLERCQ, *Ibid.*, (6), 1967-1970

Epimerisation of *cis*-1,2-dimethylcyclohexane was studied at 110-200°C. The Arrhenius plot for each metal was drawn, and increasing activity is in the order Ni, Ru, Pd, Ir and Rh.

## HOMOGENEOUS CATALYSIS

### Homogeneous and Heterogeneous Platinum-catalysed Isotopic Hydrogen Exchange in Polycyclic Aromatic Hydrocarbons

K. P. DAVIS and J. L. GARNETT, *J. Phys. Chem.*, 1971, 75, (8), 1175-1177

Exchange between aromatic compounds and D<sub>2</sub>O is catalysed by homogeneous Pt(II) and heterogeneous Pt. This was studied on naphthalene, anthracene, pyrene, diphenyl and terphenyl. The results support the general  $\pi$ -complex theory of metal catalysis.

### Kinetics of Oxidation of Ethylene by Tetrachloropalladite

O. G. LEVANDA and I. I. MOISEEV, *Kinet. Kataliz.*, 1971, 12, (3), 567-574

The kinetics of C<sub>2</sub>H<sub>4</sub> oxidation in concentrated aqueous PdCl<sub>2</sub> solutions were interpreted by a two-way mechanism. Activation parameters were determined, together with the isotope effect ( $k_{C_2H_4}/k_{C_2D_4}$ ), and the effect of ionic forces for each reaction route.

### Palladium-catalysed Reactions of 1,3-Dienes with Active Methylene Compounds: Palladium Diphosphine Complex Catalysts

K. TAKAHASHI, A. MIYAKE and G. HATA, *Chem. & Ind.*, 1971, (18, May 1), 488

Pd catalysts such as a combination of Pd acetate and (PPh<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>(PPh<sub>2</sub>)<sub>2</sub> were effective for the reactions of buta-1,3-diene with active methylene compounds to give octa-2,7-dienyl derivatives. The results show that the coordination of the ditertiary phosphines makes possible the coordination of only one molecule of the 1,3-diene to the Pd atom.

### Palladium-catalysed Reactions of Unsaturated Compounds in Non-aqueous Solvents. Reaction of Conjugated and Cumulated Diolefins with $\pi$ -Allylpalladium Halides

D. MEDEMA and R. VAN HELDEN, *Rec. Trav. Chim.*, 1971, 90, (4), 304-323

Interaction of  $\pi$ -allylpalladium halides with conjugated dienes gives new  $\pi$ -allylpalladium complexes via addition of the allyl fragment to the diene molecule. Addition takes place at the most substituted C atom in the  $\pi$ -allyl fragment. Low molecular weight 1,2 polymers of butadiene may be formed using this complex.

### The Oligomerisation of Butadiene Using $\pi$ -Allylpalladium Acetate as Catalyst

*Ibid.*, 324-342

With  $\pi$ -allylpalladium acetate, butadiene is converted to *n*-dodecatetraene. If PPh<sub>3</sub> is added the dimer becomes the main product. With CH<sub>3</sub>OH as solvent, octadienyl, dodecatrienyl or hexadecatetraenyl methyl esters may be formed. The reaction mechanisms are discussed.

### Sequential Rhodium-catalysed Isomerisation and Disproportionation of 4-Vinylcyclohexene

C. J. ATTRIDGE and P. J. WILKINSON, *J. Chem. Soc., D, Chem. Commun.*, 1971, (12), 620

Quantitative conversion of 4-vinylcyclohexene into equimolar quantities of ethyl benzene and ethylcyclohexene occurs under the influence of catalytic quantities of RhCl<sub>3</sub> in ethanolic solution.

### Catalysis by Rhodium(I) in Nucleophilic Substitutions at Rhodium(III)

R. D. GILLARD, B. T. HEATON and D. H. VAUGHAN, *J. Chem. Soc., A, Inorg. Phys. Theor.*, 1971, (11), 1840-1846

The rates of halogen interchange in *trans*-(Rh(py)<sub>4</sub>X<sub>2</sub>) (X=Cl or Br) are markedly inhibited by O<sub>2</sub>, and are catalysed by primary and secondary alcohols unlike *trans*-(Rh(en)<sub>2</sub>X<sub>2</sub>) which require stronger reducing agents. The mechanisms are discussed; the active catalyst is a Rh(I) species formed via a Rh(III)-H intermediate.

**$\mu$  - Chloro -  $\mu$  - hydrido - dichlorobis(pentamethylcyclopentadienyl)di-rhodium and -iridium as Homogeneous Hydrogenation Catalysts**

C. WHITE, D. S. GILL, J. W. KANG, H. B. LEE and P. M. MAITLIS, *J. Chem. Soc., D, Chem. Commun.*, 1971, (14), 734-735

The hydrido complexes  $[\{M(C_5Me_5)_2HCl\}_2]$  ( $M = Rh, Ir$ ) react readily with 1,3-dienes to give enyl complexes. They are also good catalysts for the homogeneous hydrogenation of olefins.

**Effect of Hydroperoxides on the Isomerisation of Olefins Catalysed by a Ruthenium(II) Complex**

J. E. LYONS, *J. Chem. Soc., D, Chem. Commun.*, 1971, (11), 562-563

The rate of olefin isomerisation catalysed by  $RuCl_2(PPh_3)_3$  is greatly accelerated in the presence of small amounts of hydroperoxides which convert the Ru complex into a catalytically active compound having a CO ligand.

**Homogeneous Hydrogenation of Mono- and Diolefins in the Presence of Complexes of Ruthenium with *N*-Phenylalanine**

E. F. LITVIN, L. KH. FREIDLIN, K. G. KARIMOV, M. L. KHIDEKEL' and V. A. AVILOV, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1971, (7), 1539-1541

Ru complexes of *N*-phenylalanine are more selective catalysts for paraffin formation during diene hydrogenation than  $Ru/C$ .

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Microstructures of Sputtered Platinum Silicide Films

H. N. S. LEE, F. B. KOCH and W. R. COSTELLO, *Extended Abstr., 139th Natl. Mtg., Electrochem. Soc.*, 1971, (May), 171-173

The effects of sputtered deposition variables on the microstructures of PtSi films were studied. Substrate temperature is a dominant factor in determining surface microstructure; higher substrate temperatures produce smoother film surfaces. Pt whisker growth was observed in samples prepared with no continuous back sputtering. Annealing at 500°C is required to convert all the Pt to PtSi.

## TEMPERATURE MEASUREMENT

### Modern Resistance Thermometry

W. FALLON, *Instrum. Prac.*, 1971, 25, (7), 400-405

The capability of Pt resistance sensor systems is reviewed. The reasons for using Pt, sensor construction, accuracy and resistance bridge networks are discussed. Within their temperature range of application, Pt resistance sensors are the most accurate method of sensing temperature available at present.

## NEW PATENTS

### METALS AND ALLOYS

#### Platinum Group Metal Alloys

JOHNSON MATTHEY & CO. LTD.

*British Patent* 1,238,013

*German Offen.* 1,758,549

Pt group metals, particularly Rh, Pt and Pd or their alloys, are dispersion strengthened by the addition of up to 20 at.% of at least one of the following: a lanthanide, Sc, Ti, V, Y, Zr, Hf and Ta.

#### Resistance Alloys

JOHNSON MATTHEY & CO. LTD.

*U.S. Patent* 3,561,956

Resistance wires having a high electrical resistivity are made from alloys of 74-98.5 wt.% Pd, 1-15 wt.% V and 0.5-11 wt.% Mo. From 0.5 to 8 wt.% Au may also be present.

#### Sheathed Metals

JOHNSON MATTHEY & CO. LTD.

*German Offen.* 1,621,254

A refractory metal or alloy article (not Mo or W)

is sheathed in a Pt group metal or alloy, optionally with an intermediate barrier layer of, for example, a rare earth metal carbide. Applications are stated to be stirrers, crucibles, dies etc., in contact with molten glass. This corresponds to *British Patent* 1,190,266.

#### Palladium-Vanadium Alloy

JOHNSON MATTHEY & CO. LTD.

*German Offen.* 1,758,310

An alloy of high specific resistance and low temperature coefficient of resistance has the composition 74-98.5 wt.% Pd, 1-15 wt.% V and 0.5-11 wt.% Au, Mo and/or Al.

#### Dispersion Hardened Materials

DEUTSCHE GOLD- UND SILBER-SCHNEIDANSTALT

*German Offen.* 1,783,074

Dispersion hardened materials based on Pt metals or Au alloyed with metals and other elements such as Zr, are produced in two stages. In the first stage the material is soaked at 300-800°C. During the second stage it is subjected to oxidative treatment at 800-1400°C.