

# ABSTRACTS

of current literature on the platinum metals and their alloys

## PROPERTIES

### Infrared Spectra of Carbon Monoxide Adsorbed on Alloys of the Platinum Metals. I. Investigation of Infrared Spectra of Carbon Monoxide Adsorbed on Ir-Pd Alloys of Various Compositions

N. P. SOKOLOVA, *Zh. Fiz. Khim.*, 1972, **46**, (1), 170-171

Studies of the infrared spectra of CO adsorbed on 10, 50 and 90% Ir-Pd at 30-400°C showed that introduction of 10% Ir into Pd increased its stability and heat desorption.

### Diffusivity and Solubility of Oxygen in Platinum and Pt-Ni Alloys

L. R. VELHO and R. W. BARTLETT, *Metall. Trans.*, 1972, **3**, (1) 65-72

The diffusivity and solubility of O<sub>2</sub> in Pt were calculated from measurements of the permeation of O<sub>2</sub> through heated thin walled tubes. The solubility is proportional to p<sub>O<sub>2</sub></sub><sup>3/2</sup>. The diffusivity and solubility are expressed as a function of temperature in terms of exponential equations.

### Transition from Ferromagnetism to Paramagnetism in Ni-Pt Alloys

M. J. BESNUS and A. HERR, *Phys. Lett. A*, 1972, **39**, (2), 83-84

Magnetisation measurements on 50-75 at.% Pt-Ni show that a transition from ferromagnetism to paramagnetism occurs at ~59 at.% Pt. Results indicate that these alloys may be classified as weak itinerant homogeneous ferromagnets.

### Atomic Ordering and Magnetic Hardening in Pt-Pd-Fe Alloys

S. SHIMIZU and E. HASHIMOTO, *J. Japan Inst. Metals*, 1972, **36**, (1), 53-57

Atomic ordering and magnetic hardening in Pt-Pd-Fe in the composition range 0-60 at.% Pd, 0-50 at.% Pd and 40-65 at.% Fe were studied. Optimum magnetic properties are obtained in 5 at.% Pd-Fe.

### Fabrication of Two-phase Alloys in the Ruthenium-Gold-Palladium System

R. SAVAGE and V. A. TRACEY, *Mod. Develop. Powder Metall.*, 1971, **5**, 273-286

A Ru-Au-Pd alloy was produced by infiltrating a Ru skeleton with a Pd-Au alloy or, alternatively, by liquid phase sintering of a compact of the elemental powders; both methods were carried out at 1520-1550°C. The fabrication of the alloy into wire or strip using hot and cold working treatments is described.

### Effects of Hydrogen Absorption in Palladium and Palladium-24% Silver Foils

B. DUGGAN, J. P. G. FARR, J. B. KUSHNER and M. WISE, *Nature Phys. Sci.*, 1972, **236**, (66, Apr. 3), 73-74

Thin foils of annealed Pd and 24% Ag-Pd were hydrogenated electrolytically and studied by electron microscopy. Dislocations were produced, forming tangles which caused the foils to become opaque as hydrogenation progressed. Needle-like features were found, but no rifts. Ag-Pd foils resembled Pd, but there were fewer needles and the dislocation tangles accumulated less readily. The observations support explanations of X-ray line broadening on the formation of one phase from another in terms of lattice distortion.

### Occurrence of Superconductivity in Simple Cubic (Au<sub>1-x</sub>Pd<sub>x</sub>)Te<sub>2</sub> Alloys

W. Y. K. CHEN and C. C. TSUEI, *Phys. Rev. B*, 1972, **5**, (3), 901-903

The superconducting transition temperatures (T<sub>c</sub>) and lattice parameters of metastable simple cubic (Au<sub>1-x</sub>Pd<sub>x</sub>)Te<sub>2</sub> alloys, where 0 ≤ x ≤ 0.6, were measured as a function of x. As x increases, T<sub>c</sub> goes through a minimum of 1.6K near x = 0.05, and then increases steadily to a maximum of 4.5K at x = 0.45; the lattice parameter shows a slight linear decrease as x increases. The transverse magnetoresistance for x = 0.2 saturates at ~2kG and has an unusually large value.

### Influence of the Magnetostatic Interaction of Phases on the Magnetic Properties of Powders of the Fe<sub>0.7</sub>Pd<sub>0.3</sub> Alloy

V. S. BOIDENKO, YA. S. SHUR, G. S. KANDAUROVA and L. M. MAGAT, *Fiz. Metal. Metalloved.*, 1972, **33**, (1), 54-58

The magnetic properties of powders were studied for Fe<sub>0.7</sub>Pd<sub>0.3</sub> alloy containing γ<sub>1</sub> and α phases, for the highly anisotropic γ<sub>1</sub> phase produced by corrosion of the α phase, and for a mechanical mixture of γ<sub>1</sub> with powdered Fe carbonyl similar to powdered Fe<sub>0.7</sub>Pd<sub>0.3</sub>. Comparison of results indicates the effect of magnetostatic interaction of the phases on the magnetic properties of the Fe<sub>0.7</sub>Pd<sub>0.3</sub> powdered alloy.

### Kinetic and Magnetic Properties of Alloys of the System Palladium-Iron. I. Temperature Dependence of Electrical Resistance

L. I. ABRAMOVA, G. V. FEDOROV and N. V. VOLKENSHTEIN, *Fiz. Metal. Metalloved.*, 1972, **33**, (3), 527-534

During studies of the temperature dependence of the electrical resistance of 0.5, 1.0, 1.5, 2.0, 3.0,

8.0, 20, 25, 50, 60, 75, 93, 98, 99, 99.5 at. % Fe-Pd and of pure Pd at 1.8–300K the magnetic part of the effect was isolated for alloys with up to 8 at. % Fe. The concentration dependence of the residual electrical resistance was determined for hardened and annealed alloys.

### Magnetic Properties of Finely Dispersed Nondeformed Powders of Alloys of the Fe-Pd System

Y. A. S. SHUR, N. G. ILYUSHCHENKO, V. S. BOIDENKO, G. S. KANDAUROVA and L. M. MAGAT, *Fiz. Metal. Metalloved.*, 1972, **33**, (3), 552–557

Studies of the magnetic properties and phase state of  $10\text{--}10^{-2}\mu$  Fe-Pd alloy powders with highly anisotropic  $\gamma_1$ -phase led to a mechanism for magnetic reversal in these powders.

### On the Compound PdAl and Its Alloys with Copper

L. A. PANTELEIMONOV, D. N. GUBIEVA, N. R. SEREBRYANAYA, V. V. ZUBENKO, B. A. POZHARSKII and Z. M. ZHIKHAREVA, *Vest. Moskov. Univ., Ser. II, Khim.*, 1972, **27**, (1), 70–74

PdAl was found to undergo polymorphous transformations at 560°C and 700°C. The phase diagram of the system PdAl-Cu is given.

### Anomalous Viscoelastic Behaviours of Metallic Glasses of Pd-Si Based Alloys

H. S. CHEN and M. GOLDSTEIN, *J. Appl. Phys.*, 1972, **43**, (4), 1642–1648

The viscoelastic properties of Pd-Si based alloy glasses near the glass transition temperature was studied. Results are compared with those for other types of liquid. The temperature and stress dependence of the viscoelastic behaviour of these metallic glasses closely resembles that of a low molecular weight polymer glass.

### Electronic Specific Heat of $\text{Ce}_x\text{La}_{1-x}\text{Pd}_3$ Ternary Alloys

R. D. HUTCHENS, V. U. S. RAO, J. E. GREEDAN and R. S. CRAIG, *J. Phys. Soc. Japan*, 1972, **32**, (2), 451–454

The heat capacity of the cubic  $\text{Ce}_x\text{La}_{1-x}\text{Pd}_3$  alloys was measured at 1.5–10K. The alloys consist of single phases except in the region  $0.3 \leq x \leq 0.5$ . The specific heats for  $x=1.0$  and  $x=0.8$  comply with  $C_p = \gamma T + \beta T^3$  with a high value for  $\gamma$ ; the heat capacities for the remaining compositions show marked deviations from this equation, and exhibit well-defined minima in the  $C_p/T$  vs.  $T^2$  curves in some cases. Results are discussed in terms of a model for the electronic structure of these alloys.

### Note on the Resistance Anomaly in Rh with Dilute Magnetic Impurities

H. NAGASAWA, *Solid State Commun.*, 1972, **10**, (1), 33–36

The anomaly of the temperature dependence of

the resistivity of Rh with dilute magnetic impurities is discussed on the basis of the simple Friedel's sum rule and the difference of the  $d$  electron number between the impurity and Rh.

### Electrical Resistivity of Giant Moment Systems: Ni-Rh

R. W. HOUGHTON, M. P. SARACHIK and J. S. KOUVEL, *Solid State Commun.*, 1972, **10**, (4), 369–371

Electrical resistivity measurements at 2–700K on Ni-Rh alloys, which have giant magnetic polarisation clouds, reveal a magnetic scattering behaviour differing considerably from that of giant moment Ni-Cu alloys.

### Energetics, Morphology, Crystallography, and Theory of Displacive Transformations in Near-equiatomic Niobium-Ruthenium Alloys

B. KISHORE, *U.S.A.E.C. Rept. COO-1198-807*, 1971, (Jun.), 168 pp

The displacive phase transformations in Nb-Ru alloys were studied using magnetic susceptibility, electrical resistivity, optical metallography and X-ray diffraction. Alloys containing 41–45 at. % Ru undergo a CsCl ( $\beta$ ) to f.c.t. ( $\beta'$ ) transformation on cooling to room temperature; alloys containing >46 at. % Ru exhibit a two step CsCl ( $\beta$ ) to f. c. o. ( $\beta''$ ) transformation. A model for the transformation process is developed.

### Investigation of the Ternary System Zirconium-Niobium-Ruthenium

A. L. TATARKINA, E. M. SOKOLOVSKAYA, M. V. RAEVSKAYA, I. G. SOKOLOVA and A. N. ESPOVA, *Vest. Moskov. Univ., Ser. II, Khim.*, 1972, **27**, (1), 64–69

The Zr-Nb-Ru system was studied and isothermal sections at 1600°C and 1050°C are presented.

### Thermal E.M.F. and Ettinghausen-Nernst Coefficients of Rhenium and of the Platinum Group Metals

V. F. NEMCHENKO, S. N. L'VOV, P. J. MAL'KO and V. N. DELIEV, *Fiz. Metal. Metalloved.*, 1972, **33**, (3), 540–545

The Ettinghausen-Nernst coefficient was determined during studies on the temperature dependence of the thermal e.m.f. of Re, Os, Ir and Pt at 100–1300 K.

### Experimental Determination of the Lattice Parameters of the Platinum Metals in the Temperature Range from –190 to 1709°C

R. H. SCHRÖDER, N. SCHMITZ-PRANGHE and R. KOHLHAAS, *Z. Metallkunde*, 1972, **63**, (1), 12–16

The lattice parameters of the Pt metals were measured at –189 to 1709°C. Supposed phase transformations of Rh and Ru above 1000°C were not found. The measurements were evaluated in terms of an equation of state due to Bradburn and Firth to determine the exponent of

an exponential potential. This evaluation gave equivalent results for Rh, Pd, Ir and Pt that were used successfully to calculate the melting points.

## CHEMICAL COMPOUNDS

### Crystal Structure of Platinum Tetrachloride

M. F. PILBROW, *J. Chem. Soc., Chem. Commun.*, 1972, (5), 270-271

PtCl<sub>4</sub> was studied by X-ray powder techniques. It is isostructural with α-PtI<sub>4</sub> and PtBr<sub>2</sub>; the unit cell is orthorhombic, with a=11.37, b=13.65 and c=5.95 Å.

### Two Forms of cis-Dibromodiammine-platinum

V. A. PALKIN, N. N. KUZ'MINA, V. E. GORBUNOV and O. N. EVSTAF'EVA, *Zh. Neorg. Khim.*, 1972, 17, (2), 556-557

The infra-red spectra and heat capacities of the yellow and red forms of cis-[Pt(NH<sub>3</sub>)<sub>2</sub>Br<sub>2</sub>] were studied with a view to explaining why the two modifications exist.

### The Crystal Structure of K<sub>2</sub>PtCl<sub>4</sub> and K<sub>2</sub>PdCl<sub>4</sub> with Estimates of the Factors Affecting Accuracy

R. H. B. MAIS, P. G. OWSTON and A. M. WOOD, *Acta Cryst.*, 1972, B28, (2), 393-399

The structures of K<sub>2</sub>PtCl<sub>4</sub> and K<sub>2</sub>PdCl<sub>4</sub> were determined with improved accuracy and new values for the interatomic distances are presented. Details of the various corrections applied to these measurements are given.

### Electrical Conduction Studies on the Partially Oxidised Metal-atom Chain Compounds K<sub>2</sub>Pt(CN)<sub>4</sub>Cl<sub>0.32</sub>·2.6H<sub>2</sub>O and K<sub>2</sub>Pt(CN)<sub>4</sub>Br<sub>0.30</sub>·2.3 H<sub>2</sub>O

P. S. GOMM and A. E. UNDERHILL, *J. Chem. Soc., Dalton Trans.*, 1972, (3), 334-337

The a.c. and d.c. conductivities for single crystals of K<sub>2</sub>Pt(CN)<sub>4</sub>Cl<sub>0.32</sub>·2.6H<sub>2</sub>O and K<sub>2</sub>Pt(CN)<sub>4</sub>Br<sub>0.30</sub>·2.3H<sub>2</sub>O were measured. For d.c. fields of <120 V/cm the initial conductivity in the direction of the metal-atom chain is 10<sup>-4</sup> mho/cm decreasing to 10<sup>-6</sup> with time. The conductivity perpendicular to the metal-atom chain is 100 times lower. The a.c. conductivity is similar in magnitude to the d.c. conductivity.

### Enthalpy of Ruthenium Dioxide to 1200K by Drop Calorimetry

R. FREDRICKSON and M. G. CHASANOV, *J. Chem. Engng. Data*, 1972, 17, (1), 21-22

A high-precision drop calorimetric system was used to measure, relative to 298.15K, the enthalpy of RuO<sub>2</sub> at 600-1200K. An equation for the enthalpy of RuO<sub>2</sub> at 298-1200K is given and values of (H<sub>T</sub><sup>o</sup>-H<sub>298.15</sub><sup>o</sup>), C<sub>p</sub><sup>o</sup> and (S<sub>T</sub><sup>o</sup>-S<sub>298.15</sub><sup>o</sup>) are tabulated.

## ELECTROCHEMISTRY

### Porous Platinum Electrodes

V. E. DIMITRENKO, A. A. TROFIMOVA, M. I. LAVRENT'EV, G. F. NOVIKOV and M. B. ARTEM'EVA, *Porosh. Metall.*, 1972, 11, (9), 88-93

The technology of granulation of Pt black to definite grain size powder without waste and loss was developed under laboratory conditions. The method is based on repetitive passing of the charge through a sieve followed by stage type heat treatment of the powder.

### Biogalvanic Cell

*Physics Exhibition Handbook*, 1972, 105-106

A cell which provides increased lifetimes to power sources for devices implanted in the body, e.g. cardiac pacemakers, contains a consumable Al anode and a Pt black cathode. The electrolyte is 0.9% NaCl solution which is isotonic with body fluid. In vitro a 5.5 cm<sup>2</sup> cell can deliver over 70 μW at 0.9 V for one year at room temperature.

## LABORATORY APPARATUS AND TECHNIQUE

### The Use of Platinum Black for Improved Electron Collection

J. R. LOSEE and D. S. BURCH, *Rev. Sci. Instrum.*, 1972, 43, (1), 146-147

The total secondary electron emission coefficient for Pt black on stainless steel was measured over a range of electron energies from 0 to 40eV. Also, the electron reflection characteristics for an improved Pt black screened collector are reported.

## HETEROGENEOUS CATALYSIS

### Investigation of the Sorption Properties of Platinum Black by the Conductometric Method

I. K. TOIBAIEV, T. I. YAKOVLEVA, D. V. SOKOL'SKII and D. N. DAVIDOVICH, *Zh. Fiz. Khim.*, 1972, 46, (2), 479-481

Tests of the adsorption properties of Pt black in various solvents by measurements during chemical dehydrogenation showed that the amount of H<sub>2</sub> desorbed from the catalyst depends on the temperature, the type of solvent and the unsaturated substance.

### Hydrogen Adsorption on Skeleton Platinum-Iridium Catalysts

A. D. SEMENOVA, N. V. KROPOTOVA, G. D. VOVCHEENKO and K. H. I. YANKOVSKII, *Vest. Moskov. Univ., Ser. II, Khim.*, 1972, 27, (1), 102-104

The structure and adsorptive properties of a range of skeleton Pt-Ir was studied and the differential heats of H-adsorption and the bonding energy of H with the catalyst were calculated.

### Oxidation of Ammonia-Oxygen Mixtures on Platinum in a Hardening Heterothermal Reactor

M. G. GOLOMB and P. M. STADNIK, *Kinet. Katal.*, 1971, (7), 50-54

The oxidation of  $\text{NH}_3$  by  $\text{O}_2$  on a 10% Rh-Pt catalyst without preliminary heating and at variable flow rates was studied. The degree of oxidation increased with increased  $\text{O}_2:\text{NH}_3$  ratio. In the oxidation of  $\text{NH}_3$ -air mixtures, the condensate obtained contained 180-200g/l  $\text{HNO}_3$ ; with  $\text{NH}_3\text{-O}_2$  mixtures the  $\text{HNO}_3$  content was 850-870g/l. The relation between degree of oxidation and  $\text{NH}_3$  flow rate was studied.

### Effect of Preparation on the Apparent Surface Composition of Pd-Rh Alloy Films Used for CO Oxidation

R. L. MOSS and H. R. GIBBENS, *J. Catalysis*, 1972, 24, (1), 48-56

Pd-Rh alloy films were shown by X-ray diffraction to consist of two phases in the range 30-90% Rh. Rates of CO oxidation were increased by addition of Rh. The rate of CO oxidation increased linearly with apparent surface content of Rh. This was used to estimate the surface composition of Pd-Rh alloy films prepared in other ways.

### On the Effect of Metal Particle Size on the Isomerisation of *n*-Hexane over Supported Platinum Catalysts

F. M. DAUTZENBERG and J. C. PLATTEUW, *J. Catalysis*, 1972, 24, (2), 364-365

The isomerisation of *n*-hexane over  $\text{Pt}/\text{Al}_2\text{O}_3$  containing 1,5 and 10 wt.% Pt was studied. The initial relative formation of 2- and 3-methylpentane is independent of Pt loading from 0.5 to 10 wt.% Pt and hence of metal particle size.

### Study of the Mechanism of Aromatisation of *n*-Hexane on Platinum/Alumina Catalyst

L. I. ZABOTIN and M. E. LEVINTER, *Neftekhimiya*, 1972, 12, (1), 9-13

Aromatisation activity of  $\text{Pt}/\text{Al}_2\text{O}_3$  drops during poisoning by  $\text{NH}_3$  due to reduced acidity and suppression of isomerisation of *n*- to *iso*-hexane and of dehydroisomerisation of methylcyclopentane to  $\text{C}_6\text{H}_6$ . Aromatisation of *n*-hexane occurs mainly via the formation of the intermediate methylcyclopentane on the active centres.

### Dehydrocyclisation of Paraffins. Influence of Chlorine on Cyclisation Pathway over $\text{Pt-Al}_2\text{O}_3$ Catalysts

B. H. DAVIS, *J. Catalysis*, 1971, 23, (3), 355-357

The aromatic isomer distribution for the dehydrocyclisation of 3-methylheptane over  $\text{Pt}/\text{Al}_2\text{O}_3$  with and without Cl was studied. The presence of Cl does not alter the selectivity or the reaction pathway but provides an easier methyl migration pathway. Cl added as  $\text{NH}_4\text{Cl}$

did not have as much effect as Cl added as  $\text{H}_2\text{PtCl}_6$  in the catalyst preparation; the latter is probably of a specific type.

### Aromatic Distribution from Paraffins and Naphthalenes Containing a Quaternary Carbon

B. H. DAVIS, *J. Catalysis*, 1971, 23, (3), 340-354

The aromatic product distribution from the dehydrocyclisation of paraffins containing a quaternary C atom and a 6-C chain were compared to those obtained from conversion of the naphthenes corresponding to 6-C ring formation from the paraffins. Pt and  $\text{Cr}_2\text{O}_3$  on "non-acidic"  $\text{Al}_2\text{O}_3$  were compared. Geminal dimethyl naphthenes gave similar results over  $\text{Cr}_2\text{O}_3$  and over a low isomerisation  $\text{Pt}/\text{Al}_2\text{O}_3$  catalyst. Demethylation at the quaternary C was the main reaction pathway. Over Pt dehydrocyclisation occurs by direct 6-C ring formation. The aromatic distribution is very sensitive to the method of preparation of  $\text{Pt}/\text{Al}_2\text{O}_3$ .

### Kinetics of Olefin Hydrogenation over a Platinum Catalyst with More than One Set of Active Sites

S. KOLBOE, *J. Catalysis*, 1972, 24, (1), 40-47

The hydrogenation of  $\text{C}_3\text{H}_6$  and *iso*- $\text{C}_4\text{H}_8$  over  $\text{Pt}/\text{Al}_2\text{O}_3$  is explained using a dissociative model with two types of active catalyst site. The mean deviation between calculated and observed reaction rates is less than 3%.

### Platinum-catalysed Hydrazine Reductions of Plutonium(IV) and Uranium(VI)

J. L. SWANSON, *U.S.A.E.C. Rept. BNWL-1584*, 1971, 25 pp

The use of  $\text{Pt}/\text{Al}_2\text{O}_3$  for the reduction of U(VI) to U(IV) and of Pu(IV) from irradiated reactor fuels was studied. The reaction took place in a solution of  $\text{N}_2\text{H}_4$  in  $\text{HNO}_3$  without added  $\text{H}_2$ . The effects of reaction temperature, and of the concentration of U(VI),  $\text{N}_2\text{H}_4$  and  $\text{HNO}_3$  were studied, together with catalyst stability and poisoning.

### Catalytic Selective Removal of Nitrogen Oxides from Exhaust Gases

A. P. ZASORIN, V. I. ATROSHCHENKO and O. N. KULISH, *Khim. Tekhnol. (Kiev)*, 1971, (5), 8-9

$\text{Pd}/\text{Al}_2\text{O}_3$  with  $\text{NH}_3$  was 96% effective in reducing to  $\text{N}_2$  the 0.15 vol.% NO contained in the exhaust gases. Only small amounts of  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{NO}_2$  were formed. At an O content of 3.0 vol.% a maximum NO conversion of ~55% was obtained at ~260°C.

### Determination of the Platinum Surface in Platinised Silica from the Isotherms of Chemisorption of Hydrogen

V. S. BORONIN, V. S. NIKULINA and O. M. POLTORAK, *Zh. Fiz. Khim.*, 1972, 46, (2), 463-466

The Pt surface area in  $\text{Pt}/\text{SiO}_2$  was measured by

comparing  $H_2$  chemisorption isotherms of the Pt/SiO<sub>2</sub> catalyst with that of a Pt sponge of known surface area. Results agreed with data from electron microscopy.

### Kinetics of Hydrogen Chemisorption and the Dispersion of Platinum Crystals

V. S. BORONIN, V. S. NIKULINA and O. M. POLTORAK, *Vest. Moskov. Univ., Ser. II, Khim.*, 1972, 27, (1), 24-28

The chemisorption of  $H_2$  on Pt/SiO<sub>2</sub> was studied at various degrees of Pt dispersion; at low temperatures the behaviour is in agreement with equations derived from the theory of adsorption on non-uniform surfaces. Activation energy partition functions were obtained from kinetic equations, and were dependent upon Pt dispersion.

### Mitohedral Method of Study of Active Centres of Crystalline Platinum in the Dehydrogenation of Organic Compounds

A. N. MITROFANOVA, V. S. BORONIN and O. M. POLTORAK, *Zh. Fiz. Khim.*, 1972, 46, (1), 58-62  
Studies relating the specific catalytic activity of Pt/SiO<sub>2</sub> with Pt particles of 10-400 Å to the dispersion of the Pt particles during dehydrogenation of cyclohexane, hydrogenolysis of cyclopentane and dehydrogenation of *iso*-propyl alcohol showed that the specific activity was approximately constant for Pt particles with mean size within the indicated limits. The dispersion of Pt was estimated by chemisorption of  $H_2$ .

### Hydrogenation of Organic Compounds on Ruthenium-Platinum Catalysts, Supported on Titanium Dioxide

T. V. KUZORA, D. V. SOKOL'SKII and K. K. DZHARDAMALIEVA, *Izv. Akad. Nauk Kaz. S.S.R., Ser. Khim.*, 1971, 21, (6), 14-18

The hydrogenation rate of  $Me_2C(OH)C \equiv CH$  (I),  $2-O_2NC_6H_4OH$  (II) and  $Me_2CO$  (III) on Ru-Pt/TiO<sub>2</sub> catalyst was greatest with 17.6-32.5 and 45-50 at. % Ru. For I the rate is of zero order up to 70-75% conversion, then increases sharply. With increasing Ru:Pt ratio the selectivity with respect to hydrogenation of the triple bond decreases. For II in 0.1M KOH the rate is of zero order; 32.5 at. % Ru-Pt is more active than pure Pt by a factor of 60; the reaction does not proceed on Ru. For III the reaction is first order and pure Pt or Ru are not active.

### Effect of Additions of Manganese, Chromium and Zinc on the Activity of Palladium/Alumina Catalyst in the Reactions of Hydrogenation and Dehydrogenation

O. V. ANDREEVA and R. I. IZMAILOV, *Neftekhimiya*, 1972, 12, (1), 33-36

Studies of the effects of Mn, Cr and Zn additions on the activity of Pd/Al<sub>2</sub>O<sub>3</sub> for C<sub>6</sub>H<sub>6</sub> hydrogen-

ation, dehydrogenation of cyclohexane and conversion of C<sub>6</sub> hydrocarbons indicated that Cr and Mn increase the content of adsorbed  $H_2$  and hence the activity for hydrogenation. Mn increases the activity for dehydrogenation of cyclohexane. All three additives lead to the suppression of hydrocracking of the hydrocarbons.

### Role of Hydrogen in Butene Isomerisation Catalysed by Supported and Unsupported Palladium

L. HOLBROOK and H. WISE, *J. Catalysis*, 1972, 24, (2), 315-319

The isomerisation of butene-1 is proportional to  $[H_2]^{\frac{1}{2}}$  for Pd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The distribution of butene-2 isomers initially is equal. This supports the addition-abstraction of H as an essential step for double bond migration.

### Kinetics of the Vapour-phase Dehydrogenation of Cyclohexane over Palladium Catalyst in a Continuous Stirred Tank Reactor

D. ROULEAU, D. KLVANA and J. SANG, *J. Appl. Chem. Biotechnol.*, 1972, 22, (2), 149-164

The catalytic vapour phase dehydrogenation of cyclohexane was studied over Pd/Al<sub>2</sub>O<sub>3</sub> in a continuously stirred tank reactor at 250-340°C and 0-2 atm cyclohexane.

### Hydrogenation of Cottonseed Oil in Aromatic Hydrocarbons in the Presence of a Fixed-bed Catalyst

N. G. KRUPENYA, K. A. ZHUBANOV and D. V. SOKOL'SKII, *Izv. Vysshikh Ucheb. Zaved., Pishch. Teknol.*, 1971, (4), 57-59

The hydrogenation of cottonseed oil in the presence of Ni-Al-Pd at 60-12°C and 6 atm  $H_2$  pressure went best in C<sub>6</sub>H<sub>6</sub> to give a hydrogenated fat, m.pt. 31.5-46.2°C depending on hydrogenation temperature. The activation energy for hydrogenation was 2.3 kcal/mole.

### Zeolites and Their Uses as Hydrogenation Catalysts

L. D. ZHUBANOVA, *Vestn. Akad. Nauk Kaz. S.S.R.*, 1971, 27, (10), 53-61

Pd-loaded type A zeolites were studied as hydrogenation catalysts. Changes in the structure during preparation were studied by i.r., X-ray, electron microscopy, DTA and chemical analysis methods. The NaA, KA and CaA zeolites containing  $\leq 0.6\%$  Pd were tested for hydrogenation of acetylenic alcohols, cottonseed oil and nitrobenzene. The order of catalytic activities was Pd/NaA > Pd/KA > Pd/CaA.

### Reversible Uptake of Hydrogen by Hydrocarbons Chemisorbed on Palladium

N. R. AVERY, *J. Catalysis*, 1972, 24, (1), 92-100

The reversible uptake of  $H_2$  by a hydrocarbon

residue chemisorbed on Pd/SiO<sub>2</sub> was studied. At 20–80°C the fractional saturation was proportional to  $p_{H_2}^{\frac{1}{2}}$ ; the heat of adsorption was 12.5 kcal/mole. The exchange of hydrocarbons with D<sub>2</sub> and reverse exchange with H<sub>2</sub> at 40–80°C follows first order kinetics, the activation energy being 18 kcal/mole. A potential energy diagram was constructed.

#### Conversion of Toluene during Reaction with Water Vapour on Rhodium Catalyst

L. M. TREIZER, G. L. RABINOVICH and L. N. MAS-LYANSKII, *Neftekhimiya*, 1972, 12, (1), 29–32

Dealkylation of toluene by reaction with H<sub>2</sub>O vapour over Rh/Al<sub>2</sub>O<sub>3</sub> at 400–480°C yields 50–55 mol.% C<sub>6</sub>H<sub>6</sub>. The selectivity of this reaction increases as H<sub>2</sub>O: toluene ratio decreases and as the toluene conversion increases. The rate of decomposition of C<sub>6</sub>H<sub>6</sub> during reaction with H<sub>2</sub>O vapour is 2.3–2.7 times the rate of decomposition of the aromatic ring of toluene.

#### Investigation of the Hydrogenation of Cyclohexadiene-1,4 on Rh-C Catalyst

L. K. H. FREIDLIN and I. L. POPOVA, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1972, (4), 905–909

Hydrogenation of cyclohexadiene-1,4 over Rh/C occurs in two stages – first at constant rate to cyclohexene and then to cyclohexane. Kinetic curves for the process pass through a maximum, depending on the rate of saturation of diene being lower than the constant rate of hydrogenation of the produced cyclohexene. There is some disproportionation and the C<sub>6</sub>H<sub>6</sub> formed inhibits the conversions of cyclohexadiene and cyclohexene more at higher concentrations.

#### Hydrogenation of Dimethylethynylcarbinol on Iridium Catalysts Supported on Al<sub>2</sub>O<sub>3</sub>

D. V. SOKOL'SKII, N. I. GUIALYUK and K. K. DZHARDAMALIEVA, *Zh. Fiz. Khim.*, 1972, 46, (2), 381–383

The rate of hydrogenation of dimethylethynylcarbinol over Ir/Al<sub>2</sub>O<sub>3</sub> increases linearly with the amount of catalyst and with the content of active material on the support. Hydrogenation occurs by charging the catalyst surface with H<sub>2</sub>. The catalyst mixed potential is >30mV during the reaction. Catalyst activity remained constant during repeated trials on a batch of catalyst.

#### Kinetics of Hydrogenolyses of *n*-Butane and *iso*-Butane on Supported Ruthenium

J. C. KEMPLING and R. B. ANDERSON, *Ind. Engng. Chem., Process Des. Dev.*, 1972, 11, (1), 146–151

The hydrogenolyses of *n*-butane and *iso*-butane were studied on 0.5 wt.% Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in a continuously stirred reactor at 800 torr and 85–130°C. For *n*-butane the butane order was 0.91, the hydrogen order –1.35 and the activation energy 48.1 kcal/mole; for *iso*-butane the butane

order was 0.74, the H<sub>2</sub> order –0.66 and the activation energy 36.2 kcal/mole. *n*-Butane reacted 10 times faster than *iso*-butane. A reaction mechanism is proposed in which C-C bond cleavage is the rate determining step.

#### Mechanisms of Dehydrocyclisation on Platinum and Palladium Catalysts

J. M. MULLER and F. G. GAULT, *J. Catalysis*, 1972, 24, (2), 361–364

The mechanism of the dehydrocyclisation of 2,2,4-trimethyl-, 2,2,3-trimethyl- and 2,2,4,4-tetramethylpentanes were studied over Pt and Pd films at 300°C. The results suggest that different intermediates are responsible for dehydrocyclisation on Pt and Pd.

#### Catalytic Oxidation of Some Gaseous Products from the Pyrolysis of Human Wastes

G. S. SINYAK, P. V. LISOVSKII, G. I. CHIZHIKOVA, M. A. VITASHKINA, E. I. KARPOVA, B. G. GUSAROV and L. L. ZABLOTSKII, *Kosm. Biol. Med.*, 1971, 5, (5), 77–80

The applicability of Pt and Pd catalysts for oxidation of gases formed during the thermal treatment of human wastes was studied. The oxidation reaction of the gas mixture is completed at 350°C only with Pd catalysts.

#### Semi-empirical Calculation of the Heat of Adsorption of Hydrogen on Hydrogenation Catalysts in Solutions

YU. A. PODVYAZKIN, *Zh. Fiz. Khim.*, 1972, 46, (2), 452–453

Experimental and calculated data for the differential and integral heats of adsorption of H<sub>2</sub> on Pt, Ir, Ru and Os blacks in H<sub>2</sub>SO<sub>4</sub> solutions are in good agreement.

#### Hydrogenation of Benzene in the Presence of Mixed Platinum Group Metal Catalysts

N. I. POPOV, D. V. SOKOL'SKII, F. B. BIZHANOV and ZH. G. AKCHALOV, *Zh. Fiz. Khim.*, 1972, 46, (3), 634–637

Various Pt-Ru, Pd-Ru, Rh-Ru, Pt-Pd, Pd-Rh, Pt-Rh catalysts as 0.5 wt.% supported on Al<sub>2</sub>O<sub>3</sub> were tested during liquid-phase hydrogenation of C<sub>6</sub>H<sub>6</sub> to determine the connection between their activity and their composition during intensive mixing of the reactants.

#### Alkyl Transfer Steps in the Catalytic Alkylation of Benzene, Toluene, and Cyclohexane

G. FARRAVANO, *J. Catalysis*, 1972, 24, (2), 233–240

The rate of the catalytic redistribution of <sup>14</sup>C in binary mixtures of PhH, PhCH<sub>3</sub>, PhC<sub>2</sub>H<sub>5</sub>, Ph(CH<sub>3</sub>)<sub>2</sub> and cyclohexane was investigated over supported Pt, Ir, Ru and Au. The effect of pressure, temperature, catalyst support, catalyst acidity and preparation method were studied.

## HOMOGENEOUS CATALYSIS

### Formation of Palladous Acetate and Stability of Catalyst in Palladium-metal-catalysed Synthesis of Vinyl Acetate from Ethylene

S. NAKAMURA and T. YASUI, *J. Catalysis*, 1971, **23**, (3), 315-320

Pd catalysed synthesis of vinyl acetate from  $C_2H_4$  was studied. Pd(II) acetate was formed only with high partial pressures of acetic acid and  $O_2$  and at low temperatures. It may cause aggregation of Pd on the catalyst surface, thus lowering the activity.

### Homogeneous Hydrogenation of Methyl-*cis*-9,*cis*-15-octadecadienoate Catalysed by Platinum-Tin, Palladium and Nickel Complexes

E. N. FRANKEL, H. ITATANI and J. C. BAILAR, *J. Am. Oil Chem. Soc.*, 1972, **49**, (2), 132-133

Methyl-*cis*-9, *cis*-15-octadecadienoate was used as a model for the hydrogenation of methyl linolenate. Catalysis by  $H_2PtCl_6$ ,  $PtCl_2(PPh_3)_2$ ,  $PtCl_2(Ph_3As)_2$  with  $SnCl_2$  and by  $Pd(CN)_2(PPh_3)_2$  produced a mixture of isomeric monoenes similar to that from the hydrogenation of methyl linolenate. These catalysts promote isomerisation of double bonds to give conjugated dienes necessary for monoene production.

### Polymerisation of Isoprene and 2,3-Dimethyl-1,3-butadiene in an Allyl Alcohol Medium in the Presence of Rhodium Trinitrate Dihydrate

A. ENTEZAMI, A. GERAUDELLE, F. KAUFMANN, F. SCHUE, A. DELUZARCHE and A. MAILLARD, *Eur. Polymer J.*, 1971, **7**, (7), 889-911

Isoprene and 2,3-dimethyl-1,3-butadiene were polymerised in the presence of  $Rh(NO_3)_3 \cdot 2H_2O$  in  $C_6H_6$  and allyl alcohol to give polyisoprene and poly(2,3-dimethyl-1,3-butadiene), with a predominantly 1,4-*cis* configuration.

## CHEMICAL TECHNOLOGY

### Study of the Corrosion of the Alloy of Titanium with 0.2% Palladium in Hydrochloric Acid by the Method of Radioactive Indicators

A. A. UZBEKOV, I. V. RISKIN, Z. I. LADOZHINA and N. D. TOMASHOV, *Zashchita Metallov*, 1972, **8**, (1), 8-14

0.2%Pd-Ti alloy in 20% HCl at room temperature undergoes a Pd loss at the surface during circulation of the samples in the solution. The loss is caused by mechanical removal of Pd accumulated at the surface. Passivated samples lost no further Pd in aerated solutions but Pd continued to be dissolved at all times in deaerated solutions. It is suggested that Pd dissolves only after the Pd accumulated at the surface as Pd or  $Ti_2Pd$  is removed at a positive potential.

### Effect of Ruthenium on the Corrosion Behaviour of Titanium

N. D. TOMASHOV, T. V. MATVEEVA and YU. M. IVANOV, *Zashchita Metallov*, 1972, **8**, (2), 174-177  
Tests on Ru-Ti alloys in HCl and  $H_2SO_4$  showed that the addition of small amounts of Ru reduces the rate of corrosion of Ti.

### On the Crevice Corrosion of Titanium and Its Alloys with Palladium in Hydrochloric Acid Solutions

I. V. RISKIN, Z. I. LADOZHINA and N. D. TOMASHOV, *Zashchita Metallov*, 1972, **8**, (2), 177-181

Corrosion rates for Ti and 0.2% Pd-Ti were measured in HCl solutions at various temperatures when aerated and when deaerated. The alloy has greater resistance to crevice corrosion.

### Corrosion of Type 430 Stainless Steel: Effects of Mo-Pd and other Addition Pairs

Y. S. AGARWALA and G. J. BIEFER, *Corrosion*, 1972, **28**, (2), 64-74

Anodic and cathodic polarisation was measured at ambient in 1N  $H_2SO_4$  with and without 0.5N NaCl on Type 430 ferritic stainless steels containing addition pairs of Mo, V or W with each of Pd, Ge or Re. Mo-Pd showed the best corrosion behaviour at lower acid concentrations. In steels containing 3% Mo and 1-2% Pd, and 2% Mo and 1% Pd large regions of spontaneous passivity were observed in 25%  $H_2SO_4$  in 1N  $H_2SO_4$  Mo-Pd containing steels were shown to passivate with up to 3% NaCl additions. Surface deposits of Pd on Pd-free steels produced steels which passivated spontaneously in 1N  $H_2SO_4$ .

## GLASS TECHNOLOGY

### Mechanical and Viscoelastic Properties of Alloy Glasses

M. GOLDSTEIN and H.-S. CHEN, *U.S. Rept. AD 728,048*, 1971, 22 pp

Glasses of the general formula  $Pd_xAu_ySi_z$ ,  $Pd_xAg_ySi_z$ ,  $Pd_xCu_ySi_z$  and  $Ni_xPd_yP_z$  were prepared. Their inelastic and viscoelastic properties and their flow fracture behaviour are reported.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Equivalent Circuit for Conductivity-Temperature Characteristics of the PdO/Ag-Pd Glaze Resistor

G. J. KAHAN, *IBM J. Res. Develop.*, 1971, **15**, (4), 313-317

The conductivity of PdO/Ag-Pd glaze resistors measured at 80-450°C does not exhibit the intrinsic conductivity regime seen in PdO. A new model is proposed which assumes a two-phase mixture of metal and semiconductor.

## Rheology of Pastes in Thick-film Printing

R. E. TREASE and R. L. DIETZ, *Solid State Technol.*, 1972, **15**, (1), 39-43

The rheological behaviour of thick film pastes including Pd-Au and Pd-Ag compositions was measured and the results correlated with printing parameters. Two methods of relating paste viscosities to performance are described. A series of thick film pastes were tested at equilibrium and non-equilibrium conditions over a range of shear rates. The results show the danger of adjusting paste formulations using simple viscosity measurements.

## TEMPERATURE MEASUREMENT

### Estimation of the Effect of Uncontrolled Additions on the Electrical Resistivity of Platinum in Resistance Thermometers

YA. I. DUTCHAK, V. YA. PROKHORENKO and N. A. SKORODINSKII, *Teplofiz. Vysokikh Temp.*, 1972, **10**, (1), 198-202

The effects of various construction materials on the resistivity parameters of Pt resistance thermometers are shown in tabular form.

# NEW PATENTS

## METALS AND ALLOYS

### Resistance Alloys

JOHNSON MATTHEY & CO. LTD.

*British Patent* 1,263,454

A resistance alloy contains 26-60 wt.% Ag, 0.01-2.0 wt.% B or C; or Ir, Re or Mo; or Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> or MoS<sub>2</sub>, the balance being Pd.

### Superconductive Alloys

SIEMENS A.G.

*British Patent* 1,264,298

Superconductive alloys have the general composition: (Ce<sub>1-x</sub>A<sub>x</sub>)Ru<sub>2</sub> where A is Tb, Dy or Ho, and 0.10 ≤ x ≤ 0.24 for Tb, 0.12 ≤ x ≤ 0.27 for Dy and 0.10 ≤ x ≤ 0.28 for Ho.

### Process of Preparing Noble Metal Powders

E. I. DU PONT DE NEMOURS & CO.

*U.S. Patents* 3,620,713 and 3,620,714

Acid chloride solutions of noble metals are prepared, the metal is precipitated as a metal ammonia complex and then is reduced to yield a relatively coarse noble metal precipitate powder. Metallisation compositions containing the noble metal powders are printed and fired to form various electrical circuit components. Au, Ag and Pt metal powders may be produced in this way. *U.S. Patent* 3,620,714 deals with metal alloy powders.

### Improved Platinum Alloy

DEUTSCHE GOLD- & SILBER-SCHNEIDANSTALT

*U.S. Patent* 3,622,310

The high temperature strength properties of noble metals, particularly Pt, are improved by adding an element having an affinity for O<sub>2</sub>, preferably Zr, and heating either (1) at 800-1,200°C or (2) stepwise heating at 300-800°C followed by heating at 800-1,400°C.

## CHEMICAL COMPOUNDS

### Producing Palladium-Carbon Bond Compounds

UNION CARBIDE CORP.

*U.S. Patent* 3,632,824

Reactive compounds of Pd containing Pd-C bonds are made by reacting Pd in the zero valent state with a halogen compound containing a C bond. The compounds have utility as intermediates and as catalysts. Thus Pd(PPh<sub>3</sub>)<sub>4</sub> reacts with MeI to give (PPh<sub>3</sub>)<sub>2</sub>Pd(Me)I.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Light-sensitive Composition

MINNESOTA MINING & MANUFACTURING CO.

*British Patent* 1,263,715

A composition for use in an electroless-plating light-image-recording system includes one or more diazonium salts which will undergo photolysis when exposed to light and one or more Pd compounds which are reduced by the action of the photolysis products to Pd metal. The metal acts as a catalyst in the reduction of developer.

### Electrodeposition of Ruthenium

SEL-REX CORP.

*U.S. Patent* 3,630,856

Thick electrodeposits of Ru can be obtained by adding Ga, In or Tl in a stable and soluble form. The deposits obtained have low stress and no surface cracks at thicknesses up to about 10 mm.

### Platinum Metal Alloy Coatings

KLINGSPOR & CO. INDUSTRIE-EXPORT K.G.

*German Offen.* 2,014,406

Pd alloy coatings are deposited from a bath containing, per litre, 0.05-10 g PdCl<sub>2</sub>, 1-60 g