

# ABSTRACTS

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

### PROPERTIES

#### The Construction of a Mathematical Model of the Creep Rate of Platinum-Rhodium Alloys

F. S. NOVIK, I. I. NOVIKOV, E. I. RYTVIN and S. S. PRAPOR, *Izv. vysshikh Ucheb. Zaved., tsvet. Metall.*, 1969, 12, (6), 109-115

Calculations were made on 4, 7, 11 and 15% Rh-Pt alloys.

#### Fibre Texture Formed on Transformation from Disordered F.C.C. Phase to Ordered F.C.T. Phase under Load

S. SHIMIZU and S. HORIUCHI, *Metall. Trans.*, 1970, 1, (1), 330-331

A uniaxial magnetic anisotropy was induced in 50 at.% Pt-Co tempered under compression owing to the fibre texture formed during tempering. The fibre texture was studied by X-ray diffraction. Under compression, nuclei of the ordered phase form with the preferred orientation in the early stages of ordering and grow to form the fibre texture through subsequent uncompressing tempering.

#### Iron-Platinum Hardening in Casting Golds for Use with Porcelain

D. L. SMITH, A. P. BURNETT, M. S. BROOKS and D. H. ANTHONY, *J. dent. Res.*, 1970, 49, (2), 283-288  
Fe-Pt additions to Au dental alloys promote hardening. The alloys can be solution heat-treated at temperatures used to fuse porcelains and they then precipitate-harden during slow air cooling. The hardening mechanism seems to involve the reaction  $FePt_3 \rightleftharpoons FePt$ . The precipitation varies with casting temperature.

#### Stress Directed Ordering of Pt-Co

J. PAULEVE and P. EURIN, *Phys. Status Solidi*, 1970, 37, (2), K129-K132

Large Pt-Co single crystals containing a single ordering direction have been obtained by the application of either a magnetic field or a compressive stress at the onset of ordering. The technique is applicable to other binary alloys in which the lattice undergoes a tetragonal change from disordered to ordered state.

#### Magnetic Properties and Microstructure of Cobalt-Platinum-Iron Alloys

V. I. GORBUNOV, YU. A. GRATSIANOV and B. S. KRASNOPEVTSOV, *Metall. term. Obrabot. Metal.*, 1970, (2), 13-16

The magnetic properties of Co-Pt alloys con-

taining 50 at.% Pt are tabulated and compared with those of alloys where Co is replaced by 10, 20 and 30 at.% Fe.

#### Coercivity and Structure of Fe-Pt Alloys

L. M. MAGAT, G. V. IVANOVA, L. V. SOLINA, N. N. SHCHEGOLEVA and YA. S. SHUR, *Fiz. Metal. Metalloved.*, 1970, 29, (2), 400-403

Maximum coercivity in equiatomic Fe-Pt alloy occurs in the single phase ordered state. The size of the tetragonal phase crystals, with a crystalline anisotropy magnetic constant of the order of  $10^7$  erg/cm<sup>3</sup>, is the basic factor determining the value of the coercivity.

#### The Thermodynamic Properties of Some Pt-Cr Alloys in the Temperature Range 1450 to 1550°C

D. A. R. KAY and A. K. MOHANTY, *Metall. Trans.*, 1970, 1, (1), 303-304

The activity-composition relationship in Pt-Cr alloys was determined in this range. Results were expressed in terms of the excess free energy of mixing  $\Delta G_{\chi}^E/4.575 T \approx \chi_{Cr}(1-\chi_{Cr}) [B+C(2\chi_{Cr}-1)]$ . Values of B were -4.50, -4.22 and -3.68, and of C were 0.08, 0.12 and 0.42 at 1450, 1500 and 1550°C respectively.

#### Structure and Superconductivity of Ternary Molybdenum-Platinum-Rhenium Alloys

E. RÖSCHEL and E. RAUB, *Z. Metallkunde*, 1970, 61, (1), 71-76

Studies of Mo-rich Pt-Mo-Re alloys at 1050, 1600 and 1800°C revealed only phases found in the binary systems. Re stabilised the A15 Mo-Pt phase to higher and lower temperatures. The transition temperature to superconductivity agreed generally with measurements on Mo-Pt and Mo-Re alloys. It was not increased by A15-phase formation in the ternary alloys; it increased with Re content but did not exceed that for saturated A2 solid solution. Transition temperature in the A2-phase decreased with increasing Pt content at constant Re content. Ternary alloys with  $\sigma$  phase exhibited a minimum in transition temperature.

#### On the Ferromagnetic Intermetallic Compounds PtMnSn and PtMnSb

K. WATANABE, *J. phys. Soc. Japan*, 1970, 28, (2), 302-307

The crystal structures and magnetic properties of Pt-Mn-Sn and Pt-Mn-Sb alloys were investigated by X-ray analysis, magnetic analysis and NMR. Alloys of stoichiometric composition were ferromagnetic. PtMnSn had CaF<sub>2</sub>(Cl)-type

structure; PtMnSb had ordered MgAgAs(Cl<sub>6</sub>)-type structure. Pt<sub>1.01</sub>Mn<sub>0.99</sub>Sn<sub>1.00</sub> H<sub>2</sub>O-quenched from 1325°C or else slow-cooled had lattice parameters of 6.263 or 6.201 Å respectively at room temperature, ferromagnetic Curie temperatures of 360 and 582K, Bohr magnetons of 3.65 and 4.14 μ<sub>B</sub>/mol at OK, internal magnetic fields of 204.5 and 220.2 kOe at the Mn<sup>55</sup> nucleus at 77K.

### Diffusion and Solubility of Hydrogen in Palladium and Palladium-Silver Alloys

G. L. HOLLECK, *J. phys. Chem.*, 1970, **74**, (3), 503-511

Diffusion coefficients and heats of solution for low H<sub>2</sub> concentrations in Pd and Pd-Ag alloys were determined at 260-640°C. Change in activation energy for H<sub>2</sub> diffusion with increasing mole fraction X<sub>Ag</sub> of Ag from Pd to Pd<sub>0.5</sub>Ag<sub>0.5</sub> is represented empirically as  $E = 3800 X_{Ag}^4 + 1500 X_{Ag}^2 + 5260$  cal. The pre-exponential factor showed only a slight linear decrease. The molar heat of desorption ΔH<sub>H<sub>2</sub></sub> increased with Ag concentration from 4000 cal (Pd) to a maximum between 8020 (Pd<sub>0.6</sub>Ag<sub>0.4</sub>) and 7090 cal (Pd<sub>0.5</sub>Ag<sub>0.5</sub>). Entropy of desorption ΔS<sub>H<sub>2</sub></sub> remained steady at 23.3-24.4 cal/deg mol.

### Electrical Resistivity of PdH<sub>x</sub> System for H/Pd Atom Ratios to 0.97

R. J. SMITH and D. A. OTTERSON, *J. Phys. Chem. Solids*, 1970, **31**, (1), 187-189

The resistivity of PdH<sub>x</sub> has been measured at 4.2 and 270K for x up to 0.97. Results are presented in graphical form relating resistivity to H<sub>2</sub> absorption and are discussed in terms of the Bambakidis, Smith and Otterson model.

### Theoretical Aspects of the Absorption of Hydrogen by Palladium and its Alloys. Part 1. A Reassessment and Comparison of the Various Proton Models. Part 2. Possible Effects of Lattice Expansion on the Solubility of Hydrogen in Palladium

R. BURCH, *Trans. Faraday Soc.*, 1970, **66**, (3), 736-748, 749-755

A model is developed which takes account of possible changes in strain energy as a function of H<sub>2</sub> content when H<sub>2</sub> is absorbed by Pd. The model predicts a limiting solubility at H/Pd < 1.0 and a minimum heat of solution of H<sub>2</sub> at H/Pd < 0.6, in agreement with experimental results.

### The Diffusion of Hydrogen in Boron-Palladium Alloys

K. D. ALLARD, T. B. FLANAGAN and E. WICKE, *J. phys. Chem.*, 1970, **74**, (2), 298-305

Diffusion of H<sub>2</sub> in Pd-B alloys was studied using electrochemical methods. Value of the diffusion coefficient for H: Pd → O declined steadily with B

content from that of pure Pd. This is in marked contrast to substitutional alloys of Pd. This supports the view that B occupies interstitial sites.

### Absorption of Hydrogen by Palladium + Boron and Palladium + Silver + Boron Alloys

R. BURCH and F. A. LEWIS, *Trans. Faraday Soc.*, 1970, **66**, (3), 727-735

The solubility of H<sub>2</sub> in some Pd+B and Pd+Ag+B alloys was determined from experimental measurements in aqueous solutions. Information was also obtained on relationships between electrical resistance and H<sub>2</sub> content. Results are discussed with respect to alternative models proposed to account for the pressure-composition isotherms of the Pd+H and Pd alloy+H systems.

### Electrical Resistivity of the Dilute Pd-Co System

G. WILLIAMS, *J. Phys. Chem. Solids*, 1970, **31**, (3), 529-539

Resistivity studies of < 1 at.% Co-Pd alloys at 0.45-300K showed that, at well below the ordering temperature, incremental resistivity followed a T<sup>3/2</sup> limiting behaviour, theoretically due to s-electron scattering in the coupled d-band. Just below the ordering temperature occurred a linear decrease of incremental resistivity with decreasing temperature. s-Electron coupling strengths and d-electron local moment coupling strengths were evaluated and compared for several Pd-Co and Pd-Fe alloys.

### Electrical Resistivity of Amorphous Ni-Pd-P Alloys

P. MALTREPIERRE, *J. appl. Phys.*, 1970, **41**, (2), 498-503

Electrical resistivity measurements of amorphous Ni-Pd-P alloys at 4.2-850K showed a Kondo effect below 15K; resistivity increased with T<sup>2</sup>, and then linearly up to 550K. Above 570K the amorphous alloy transformed progressively into crystallite phases. The small temperature coefficient of resistivity, 10<sup>-4</sup>/deg C, was attributed to the high degree of structural disorder in the amorphous state. Variation of resistivity with temperature in specimens heated at 1.5 deg C/min is correlated with structural changes observed by X-ray diffraction.

### Martensitic Transformations in Gold-Titanium, Palladium-Titanium and Platinum-Titanium Alloys near the Equi-atomic Composition

H. C. DONKERSLOOT and J. H. N. VAN VUCHT, *J. less-common Metals*, 1970, **20**, (2), 83-91

These alloys are B19-type orthorhombic at room temperature and B2-type Cs-type at high temperatures. Martensitic transformations were studied by X-ray diffraction and the composition dependence of the transformation characteristics

were determined. Lattice constants of the high temperature phases are given.

### Experiments on Deep-drawing of Rhodium Cups at 300 to 500°C

G. REINACHER, *Z. Metallkunde*, 1970, **61**, (3), 201-205

An electrically heated tool for cup drawing up to 600°C makes it possible to obtain Rh cups 31 mm × 33 mm diam. at 350-500°C in one drawing from 0.3 mm × 70 mm diam. discs whereas hot rolling is possible only above 1000-1200°C. Increase in deep-drawing capability at 350°C is marked by a corresponding increase in elongation and reduction of area.

### The Alloys of Nickel with Iridium and Rhodium

E. RAUB and E. RÖSCHEL, *Ibid.*, (2), 113-115

The alloys of Ni with Ir and Rh were investigated by X-ray diffraction and microscopy. These systems possess continuous solid solutions. Decomposition reactions could not be detected nor the formation of superlattice phases.

### The Nd-Rh System

P. P. SINGH and A. RAMAN, *Metall. Trans.*, 1970, **1**, (1), 233-237

The phase diagram of the Nd-Rh system was determined by powder X-ray diffraction, metallographic and differential thermal analysis techniques. Eight intermediate phases: Nd<sub>4</sub>Rh, Nd<sub>3</sub>Rh, Nd<sub>3</sub>Rh<sub>3</sub>(l), Nd<sub>4</sub>Rh<sub>3</sub>(h), NdRh, NdRh<sub>2</sub>, and NdRh<sub>3</sub>, and Nd-19.5 at.% Rh similar to La<sub>3</sub>Rh. Intermediate phases are discussed and compared with those of the La-Rh, Nd-Co and Nd-Ni systems.

### Magnetic Properties of F.C.C. Fe-Ir Alloys

T. MIZOGUCHI and T. SASAKI, *J. Phys. Soc. Japan*, 1970, **28**, (2), 532

Fe-Ir alloys are f.c.c. up to 70% Fe but have a small amount of mixed h.c.p. phase in Fe<sub>70</sub>Ir<sub>30</sub>. Susceptibility measurements from 4.2K to ambient in fields up to 10 kOe showed magnetisation  $\propto$  field at all temperatures and for all specimens except Fe<sub>70</sub>Ir<sub>30</sub>. For Fe<sub>30</sub>Ir<sub>70</sub> a broad maximum occurred at 40K due possibly to some antiferromagnetic ordering. For 50, 60 and 70% Fe alloys, susceptibility was almost independent of temperature and showed no anomalies, nor did the electrical conductivity-temperature relationship. Low temperature specific heat measurements gave the value of the electronic specific heat coefficient  $\gamma \approx 50 \times 10^{-4}$  cal/mol. deg<sup>2</sup> for Fe<sub>70</sub>Ir<sub>30</sub>.

### X-ray Studies on Binary Alloys of Aluminium with Platinum Metals

L.-E. EDSHAMMAR, *Diss., University of Stockholm*, 1969, 50pp

The preparation and properties of Pt metal aluminides are reviewed. Intermediate phases

and their crystallographic constants are surveyed. Crystal structures are described and discussed. (78 references.)

### Preparation of Single Crystals of Platinum Group Transition Metals and Alloys

S. HORNFIELDT, J. B. KETTERSON and L. R. WINDMILLER, *J. crystal Growth*, 1969, **5**, (4), 289-293

A method of growing and annealing single crystals of Pt group metals and alloys includes O<sub>2</sub> treatment during annealing which helped give high residual resistance ratios. Final residual resistance ratios obtained were 2200 for Rh and 4600 for Pd crystals.

## CHEMICAL COMPOUNDS

### $\alpha$ -Platinum(II) Chloride and Platinum(III) Chloride

U. WIESE, H. SCHÄFER, H. G. V. SCHNERING, C. BRENDL and K. RINKE, *Angew. Chem., internat. Ed. En.*, 1970, **9**, (2), 158

A new modification,  $\alpha$ -PtCl<sub>2</sub>, has been prepared by heating Pt<sub>6</sub>Cl<sub>12</sub> in a small ampoule for 1-2 days at 500°C or by reacting the elements in a quartz ampoule in a temperature gradient.  $\alpha$ -PtCl<sub>2</sub> has black crystals with a reddish lustre; it is not isotopic with  $\alpha$ -PdCl<sub>2</sub>. Interplanar spacings and properties of  $\alpha$ -PtCl<sub>2</sub> are given. Pt(III) chloride has greenish-black needle-like crystals and is prepared by chlorination of Pt in a temperature gradient.

### Mixed Platinum Chalcogenides

E. D. RUCHKIN, L. A. VOSTRIKOVA and S. S. BATSANOV, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 1970, **6**, (2), 252-256

Conditions were established for the syntheses PtX+Y, PtY+X, Pt+X+Y, where X, Y are S, Se, Te. No change occurs at 500-600°C with PtX<sub>2</sub>+PtY<sub>2</sub>. PtSTe has been produced for the first time and parameters were determined for the hexagonal cells of PtSSe and PtSeTe. The effect was studied of synthesis conditions on such properties of these chalcogenides as density and electrical conductivity.

### Organoplatinum(IV) Compounds

J. S. THAYER, *Organometal. Chem. Rev. A, subj. Rev.*, 1970, **5**, (1), 53-56

A comprehensive survey of present knowledge of organoplatinum compounds, including the syntheses, spectroscopic properties and structures, and bonding of the most important complexes such as the triallylplatinum derivatives.

### Free Enthalpy of Formation of Rhodium Sesquioxide

H. KLEYKAMP, *Z. phys. Chem. (Frankfurt)*, 1969, **67**, (4-6), 227-283

The free enthalpy of formation of Rh<sub>2</sub>O<sub>3</sub>,

measured with the solid cell Pt|Fe, FeO|ZrO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub>|Rh, Rh<sub>2</sub>O<sub>3</sub>|Pt between 900 and 1190K and using  $\Delta C_p = -0.98 + 0.00818T + 60,000T^{-2}[\text{Cl}]$ , was found to be  $-(108,000 \pm 4,000)$  cal/mole at 298K, a result agreeing with those of other authors.

### Production and Investigation of Complexes of Divalent Ruthenium with Molecular Nitrogen

YU. G. BOROD'KO, A. K. SHILOVA and A. E. SHILOV, *Zh. fiz. Khim.*, 1970, 44, (3), 627-631

[RuN<sub>2</sub>Cl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(THF)] is formed during the reduction of RuCl<sub>3</sub>.nH<sub>2</sub>O by Zn in tetrahydrofuran solution in the presence of N<sub>2</sub>. Addition of compounds more basic than THF or H<sub>2</sub>O to the solution leads to substitution in the complex but N<sub>2</sub> is retained in it. A series of RuN<sub>2</sub>L<sub>5</sub> complexes is produced, where L=THF, H<sub>2</sub>O, (CH<sub>3</sub>)<sub>2</sub>CHO, C<sub>5</sub>H<sub>5</sub>N, CH<sub>2</sub>(NH<sub>2</sub>)<sub>2</sub>, and NH<sub>3</sub>. The infrared spectra and bonding of these complexes has been studied.

### Polynuclear Nitrido-complexes of Osmium, Ruthenium and Iridium

M. J. CLEARE and W. P. GRIFFITH, *J. Chem. Soc., A, inorg. phys. theor.*, 1970, (7), 1117-1125

The preparation and physical properties are reported of the new binuclear  $\mu$ -nitrido-complexes [M<sub>2</sub><sup>IV</sup>NX<sub>8</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>3-</sup>, where M=Os or Ru, and where X=Cl or Br; [Ru<sub>2</sub>N(NCS)<sub>8</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>3-</sup>; [Ru<sub>2</sub>N(NO<sub>2</sub>)<sub>6</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>3-</sup>; [Os<sub>2</sub>N(NH<sub>3</sub>)<sub>8</sub>X<sub>2</sub>]<sup>3+</sup>, where X=Cl, Br, I, NCS, NO<sub>2</sub>, or N<sub>3</sub>; [Ru<sub>2</sub>N(NH<sub>3</sub>)<sub>8</sub>X<sub>2</sub>]<sup>3+</sup>, where X=Cl, Br or NO<sub>2</sub>; [Ru<sub>2</sub>N(NH<sub>3</sub>)<sub>6</sub>X<sub>3</sub>(H<sub>2</sub>O)]<sup>2+</sup>, where X=Cl, NCS, or N<sub>3</sub>. Spectral studies of Os<sub>3</sub>N<sub>3</sub>(NH<sub>3</sub>)<sub>4</sub>(OH)<sub>6</sub> and of salts containing [Ir<sub>2</sub>N(SO<sub>4</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]<sup>4-</sup>, [Ir<sub>3</sub>N(SO<sub>4</sub>)<sub>6</sub>(OH)<sub>3</sub>]<sup>7-</sup> and [Ir<sub>3</sub>NCl<sub>12</sub>(H<sub>2</sub>O)<sub>3</sub>]<sup>14-</sup> are also reported.

## ELECTROCHEMISTRY

### Study of the Corrosion Resistance of a Titanium Substrate under a Platinum Coating in Relation to the pH of the Anolyte

S. D. KHODKEVICH, I. E. VESELOVSKAYA, L. M. YAKIMENKO and L. A. GUS'KOVA, *Elektrokhimiya*, 1970, 6, (1), 135-138

Polarisation curves were obtained for Pt/Ti electrodes in 0.3 and 3.0 N HCl solutions (pH 1.0 and 0), 300 g/l NaCl solution (pH 4.6), 300 g/l Na<sub>2</sub>SO<sub>4</sub> solution (pH 5.4), and pH 9.5-14.0 basic carbonate solutions.

### On the Accumulation of Palladium on Ti-Pd Alloys during their Corrosion and Self-passivation in Sulphuric Acid

N. D. TOMASHOV, G. P. CHERNOVA and T. V. CHUKALOVSKAYA, *Zashchita Metal.*, 1970, 6, (1), 3-8

Kinetics of the accumulation of Pd on Ti-Pd alloys were determined from charging curves before and after corrosion of the alloys.

### Influence of the Volume of Solution and Presence of Oxygen and Titanium Ions on the Corrosion of Titanium-Palladium and Titanium-Ruthenium Alloys

N. D. TOMASHOV, G. P. CHERNOVA and T. V. MATVEEVA, *Ibid.*, (2), 145-150

Corrosion of Ti-Pd and Ti-Ru may increase in continuously renewed boiling 5% HCl and also in 5-20% HCl, 10-40% H<sub>2</sub>SO<sub>4</sub> solution at 25°C under an atmosphere of N<sub>2</sub>. The alloys are not passivated because the cathodic process is not sufficiently effective and the concentration of Ti ions is reduced, apparently by additional oxidation.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Electrodeposition of Palladium from Chloride Electrolytes

R. K. ASTAKHOVA and B. S. KRASIKOV, *Vest. Leningrad. Univ., Ser. Fiz. Khim.*, 1969, (22), 116-123

The electrodeposition of Pd depends on the rate of stirring of the electrolyte, on the electrode polarisation, and on the concentration of Pd and Cl ions and their temperature. The kinetics of the process are explained.

## LABORATORY APPARATUS AND TECHNIQUE

### A Furnace for Growing Crystals by Vapour Phase Transport in Which Growth Can Be Continuously Observed

G. W. LORD and R. H. MOSS, *J. Phys. E, sci. Instrum.*, 1970, 3, (3), 177-179

The work tube of the furnace is made of transport SiO<sub>2</sub> wound with Pt-Rh wire on Al<sub>2</sub>O<sub>3</sub> in such a way that a viewing slit exists along most of its length, thus enabling continuous observation of the capsule in which vapour transport occurs. The furnace has low inherent stability but is screened from ambient temperature variations and its temperature is controlled up to 1100°C using a solid state temperature controller with a Pt:13% Rh-Pt sensor. Any desired temperature profile is possible over 30 cm within the limits  $\pm 0.5$  deg C for a 15 cm uniform temperature zone and a maximum temperature gradient of 15 deg C/cm.

## HETEROGENEOUS CATALYSIS

### Polishing Off Pollutants

*Du Pont Magazine*, 1970, 64, (2), 21-23

Torvex ceramic honeycomb is the support for Pt catalysts to combat air pollution, e.g., Matthey Bishop's THT catalyst. Examples of applications in diesel engine exhaust fume abatement and industrial fume removal are given.

### The Preparation of Selective Carbon Molecular Sieve Catalysts

D. L. TRIMM and B. J. COOPER, *J. Chem. Soc., D, Chem. Commun.*, 1970, (8), 477-478

C molecular sieve catalysts incorporating Pt have been prepared and show shape selectivity for olefin hydrogenation.

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

B. Y. K. PAN, *Abstr. Papers, 159th. natl Mtg, Am. Chem. Soc.*, 1970, (Feb.), PETR 28

Studies of Pt-Rh gauzes from commercial and pilot-plant reactors showed that new catalyst required 60-80 h to become activated fully and then maintained economic life for several thousand hours. Morphological change and C deposits caused specific surface area to increase with time but Fe was detrimental, 35 p.p.m. being sufficient to deactivate the catalyst.

### Aromatics-saturation Route Boasts a Better Catalyst

D. A. GAUDIO and J. E. HINES, *Chem. Engng*, 1970, 77, (7), 94-96

Process flowsheet of the Union Oil Co of California's Unisar process at Beaumont, Texas. Aromatics feedstock is hydrogenated to jet fuel at lower temperature and H<sub>2</sub> pressure than in conventional hydrotreating. Catalyst is Pt on a special support. It has high activity and is resistant to S poisoning. Its activity did not drop significantly during the first year of operation on 6000 bbl/day solvent naphthas.

### Catalytic Reforming. NPRA Questions and Answers

*Oil Gas J.*, 1970, 68, (12, Mar. 23), 58-65

The transcript of a discussion on the performance and regeneration of Pt reforming catalysts, including UOP's R-16 catalyst, Engelhard's E-501 catalyst, and Esso's Powerforming process.

### Rheniforming: a Major New Catalytic Reforming Development

A. G. EDELEANU, E. M. BLUE and C. S. MCCOY, *Erdöl Kohle*, 1970, 23, (1), 17-20

The advantages of the Chevron Pt-Re reforming catalysts are claimed to be: excellent temperature stability, no acceleration of the hydrocracking at high temperatures, the catalysts are completely regenerable. This paper presents quantitative results obtained from commercial Pt-Re catalyst units.

### Production of Benzene by Means of Severe Aromatisation of 62-85°C Fractions of Straight-run Gasoline

N. R. BURSIAK, *Khim. Tekhnol., Topliv Masel*, 1969, 14, (9), 16-19

A promoted Pt/Al<sub>2</sub>O<sub>3</sub> was developed for the

aromatisation of 62-85°C fractions at 10 atm. It gave 27 wt% C<sub>6</sub>H<sub>6</sub> when used continuously without regeneration for >1000 h. After 1300 h use for aromatisation it possessed satisfactory reduction capability in the usual oxidative regeneration conditions of Pt catalytic reforming.

### Production of High Index Oils by Hydrocracking Paraffinic Crude

V. I. KARZHEV, N. V. SHAVOLINA, V. Z. ZLOTNIKOV and I. A. VIKMAN, *Ibid.*, 1-6

Hydrocracking of vacuum distillate over Pt/Al<sub>2</sub>O<sub>3</sub> at 100-200 atm produced high-quality oils in yields up to 50%.

### Aromatisation of n-Octane in the Presence of Platinum/Alumina Catalysts

V. G. VLASOV, YU. V. FOMICHEV and B. A. KAZANSKII, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1970, (1), 64-69

Conversions were studied of n-octane, 1-methyl-2-ethylcyclopentane, n-propylcyclopentane, ethylbenzene, p-, m-, and o-xylenes in the presence of 0.6% Pt/γ-Al<sub>2</sub>O<sub>3</sub> at atmospheric pressure in a stream of H<sub>2</sub> at 300-520°C using a microreactor.

### State of the Metallic Phase of Platinum/Silica-Alumina Catalysts

F. FIGUERAS, B. MENCIER, B. AUGUIN and D. VIGNER, *C. r., Sér. C*, 1970, 270, (9), 769-771

The interactions between the metal and support were studied for a series of Pt catalysts. The kinetics of dissolution of Pt in HCl saturated with O<sub>2</sub> were used. When the support contained no oxidising centres, no dissolution was observed; when oxidising centres were present a qualitative correlation was observed between the rate of dissolution and the oxidising strength of the support.

### Catalytic Activity of Mixed Platinum-Palladium Catalysts

N. I. KOBOZEV and V. I. SHEKHOBALOVA, *Zh. fiz. Khim.*, 1970, 44, (3), 683-686

The addition of less active components to Pt+Pd catalysts for the oxidation of SO<sub>2</sub> and SO<sub>3</sub> is analogous to the action of catalyst poisons. Activation energy decreases as activity increases. The mechanism of mixed catalysts is suggested.

### Determination of Hydrogen Content on Catalysts at High Temperatures by Hydrogenation of Ethylene

R. I. IZMAILOV, G. I. FEDOROV, R. Z. KHAIRULLINA, V. V. BORISOVA and R. G. DAVLESUPOVA, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1970, (2), 369-372

A method to determine the sorption of H<sub>2</sub> at high temperatures of C<sub>2</sub>H<sub>4</sub> hydrogenation is proposed. Promotion of Pt and Pd catalysts by Mn and Cr salts strengthens the metal-H<sub>2</sub> bonds.

## Catalytic Oxidation. I. The Oxidation of Ethylene over Pd and Pd-Au Alloys

H. R. GERBERICH, N. W. CANT and W. K. HALL, *J. Catalysis*, 1970, **16**, (2), 204-219

Kinetics were determined for  $C_2H_4$  oxidation over Pd and Pd-Au in a steady-state flow reactor and in a recirculating reactor. Initial selectivity for partial oxidation was 25-45% depending on reaction conditions; steady-state values were 6-25%. Both total rate and selectivity increased with  $p_{O_2}$ . Poisoning by reaction products may have occurred. Reaction studies were assisted by using  $D_2$ ,  $^{14}C$  and  $^{18}O_2$ .

## II. Silica Supported Noble Metals for the Oxidation of Ethylene

N. W. CANT and W. K. HALL, *Ibid.*, 220-231

Oxidations of  $C_2H_4$  and  $C_3H_6$  over  $SiO_2$ -supported Pt, Pd, Ir, Ru and Rh showed specific activities falling in that order. Partial oxidation products were characterised in each case. Rate of total oxidation decreased with  $p_{olefin}$  and increased with  $p_{O_2}$  over Pt and Pd; rate increased with  $p_{olefin}$  and was inhibited by  $O_2$  over Rh and Ir; rate increased with  $p_{O_2}$  but was independent of  $p_{olefin}$  over Ru. Order of activity depended on ability of the metal to activate  $O_2$ .

## The Formation, Structure and Activity for Formic Acid Dehydrogenation of Evaporated Pd-Au Alloy Films

J. K. A. CLARKE and E. A. RAFTER, *Z. phys. Chem. (Frankfurt)*, 1969, **67**, (4-6), 169-177

Alloy films of Pd-Au were prepared by simultaneous vacuum evaporation of the component metals. Catalysis of HCOOH dehydrogenation showed a decrease in apparent activation energy with increasing Pd content, which was followed by a sharp rise to the value for pure Pd. This is believed to be due to changes in the predominance of crystal face at the catalyst surface.

## The Oxidation of Ethylene over Evaporated Palladium-Rhodium Alloy Films. I. Film Structure with Special Reference to Phase-separation

R. L. MOSS, H. R. GIBBENS and D. H. THOMAS, *J. Catalysis*, 1970, **16**, (1), 117-125

Pd-Rh slowly evaporated on glass at 400°C shows good bulk homogeneity at 0-30 and 80-100% Rh but tends to separate into two f.c.c. phases at 30-80% Rh. Phase I is deficient in Rh but Phase II is 88±5% Rh. Mechanisms for oxidation of  $C_2H_4$  in each range of catalyst composition are proposed.

## II. Variation of Activity with Film Composition and Structure

*Ibid.*, (2), 181-188

The complex variation of the rates of  $CO_2$  formation with the alloy composition during  $C_2H_4$  oxidation in a static system over Pd-Rh films reflects variations in activation energy E with

composition. 0-30% Rh-Pd do not show more activity than Pd but a minimum activity occurs at 10-15% Rh. Two alternative explanations for this are suggested. Activity decreased with increasing Rh content in 30-80% Rh-Pd alloys composed of two phases. Some enrichment of the surface by Pd may occur in 80-100% Rh-Pd alloys but activity decreases above 98% Rh to a very low level.

## Conversion of Vinylcyclohexene on Palladium Catalyst

G. G. GARIFZYANOV, I. KH. BIKBULATOV and R. B. VALITOV, *Neftekhimiya*, 1970, **10**, (1), 28-33

A scheme was established for the conversion of 4-vinylcyclohexene-1 on 0.8-1.2 wt% Pd/C at 135-210°C and for various contact times. The conversion occurred in stages; migration of double bonds occurred during both dehydrogenation and hydrogenation. Ethylcyclohexene, formed as an intermediate, breaks down to form ethylbenzene and ethylcyclohexane.

## Relation of the Activity and Stability of Palladium Catalysts Supported on Polyvinyl Alcohol to the Conditions of Preparation

O. A. TYURENKOVA and L. A. CHIMAROVA, *Zh. fiz. Khim.*, 1970, **44**, (1), 88-92

Pd/PVA catalysts were prepared by reduction from various solvents:  $H_2O$ , 50% glycerine solution, diethyleneglycol, and  $C_2H_5OH$ . Catalysts prepared using  $C_2H_5OH$  were more active, possessed better stability, and had increased selectivity. Catalyst prepared at 40°C had higher activity than that prepared at room temperature but no more than that prepared at 60°C. Increasing the temperature lowered selectivity and induced self-poisoning. Catalyst stabilities were about the same over two months.

## Hydrogenation of Dimethylethynylcarbinol on Palladium/Polyvinyl Alcohol Catalyst

*Ibid.*, (2), 375-378

The hydrogenation was studied by potentiometry in  $H_2O$ ,  $C_2H_5OH$  and in the presence of  $C_5H_5N$ . Colloidal Pd/PVA in  $H_2O$  was poisoned during successive hydrogenations by the reaction products. When coating the polymer with Pt, the maximum activity on solid and colloidal catalysts occurred when weight of polymer : metal = 12.5 : 1.  $C_5H_5N$  reduced the rate of hydrogenation of double bonds more than of triple bonds. The reaction rate passed through a maximum at low poison concentrations.

## Kinetics and Isotope Effect of Ammonia Synthesis over Ruthenium

K.-I. AIKA and A. OZAKI, *J. Catalysis*, 1970, **16**, (1), 97-101

Rate equation  $R = kP_{N_2}P_{H_2}^{\circ}P_{NH_3}^{\circ}$  was obtained for  $NH_3$  synthesis over 5 wt% Ru/Celite at 346-410°C under reduced pressure. Rate of

synthesis is presumed due to control by dissociative adsorption of  $N_2$ .  $D_2$  isotope effect over Ru was hardly detected.

### Hydrogenolysis of *n*-Butane on Supported Ruthenium

J. C. KEMPLING and R. B. ANDERSON, *Ind. engng Chem., process Des. Dev.*, 1970, 9, (1), 116-120

The hydrogenolysis of *n*- $C_4H_{10}$  was studied over 0.5 wt% Ru/ $\gamma$ - $Al_2O_3$ . The activation energy of the reaction was 48.1 Kcal/mole at 800 mm Hg, 85-120°C.

### Equilibrium Hydrogen Transfer between Benzene and $C_6$ Hydrocarbons over Supported Metal Catalysts

G. PARRAVANO, *J. Catalysis*, 1970, 16, (1), 1-15

A kinetic method for study of hydrocarbon-surface interaction during catalytic conversion of hydrocarbons involves study of the rate of redistribution of an isotope tracer between hydrocarbon molecules in thermodynamic equilibrium with the catalyst surface, e.g., H transfer between cyclohexane and other  $C_6$  hydrocarbons, and  $C_6H_6$  over Pt, Pd, Ir, Ru and Rh on  $Al_2O_3$  or  $SiO_2$  at 117°C. The relative activity was Pt > Pd > Ir > Ru > Rh.  $H_2$  surface coverage was influenced by particle size for 12-2000 Å Pt crystallites. A hydrocarbon reaction efficiency sequence was established. The nature of the reactive metal surface and the adsorbed  $H_2$  is indicated.

### Reactions of Neopentane on Transition Metals

M. BOUDART and L. D. PTAJ, *Ibid.*, 90-96

Rates  $r_H$  of hydrogenolysis of neopentane over  $SiO_2$  supported Ru, Rh, Os, Ir and Pd, Spheron-supported Pt, and Au powder at 250°C differ by ten orders of magnitude when referred to unit surface area of metal. Ru is most active; Au is least active. Of all Group VIII metals, Cu and Au, only Ir, Pt and Au isomerise neopentane to isopentane.

## HOMOGENEOUS CATALYSIS

### Organic Syntheses by Means of Noble Metal Compounds

J. TSUJI, *Advan. org. Chem.*, 1969, 6, 109-255

A review of the use of olefin-Pd complexes as intermediates in preparative chemistry and of the use of Pt complexes for resolution of enantiomeric olefins and sulphoxides. 346 references up to the end of 1966 and a supplemental list of more recent work.

### General Features of Homogeneous Catalysis with Transition Metals

R. UGO, *Chim. e Ind.*, 1969, 51, (12), 1319-1331

Four catalytic steps are important: co-ordination unsaturation, metal ion activation, ligand acti-

vation by co-ordination, template ligand reactions. These are discussed with reference to Pt, Pd, Rh, and Ru complexes, among others, which are used to catalyse, for example,  $C_2H_4$  oxidation or dimerisation.

### The Homogeneous Palladium-catalysed *ortho*-Chlorination of Azobenzene

D. R. FAHEY, *J. Chem. Soc., D, Chem. Commun.*, 1970, (7), 417

The first reported example of a homogeneous co-ordination-catalysed chlorination is that of the *ortho*-positions of azobenzene with  $Cl_2$  in the presence  $PdCl_2$ , possibly via the addition of  $Cl_2$  to a 2-(phenylazo)phenylpalladium complex.

### Palladium(II)-catalysed Synthesis of Allylic Esters

D. G. BRADY, *Ibid.*, 434-435

Displacement of  $Cl^-$  from allylic centres by  $CH_3COO^-$  is markedly catalysed by  $Pd Cl_2$ .

### The Chemistry of Palladium Complexes. VI. Studies on the Palladium(II)-catalysed Decomposition of Vinyl Acetate

R. G. SCHULTZ and P. R. RONY, *J. Catalysis*, 1970, 16, (2), 133-147

Studies of the kinetics and mechanism of the decomposition of vinyl acetate to  $CH_3CHO$  and acetic anhydride, catalysed by  $PdCl_2$  in  $CH_3COOH$  in the presence and absence of excess chloride, nitrile, and  $H_2O$  as promoters or inhibitors of decomposition, enabled rate constants to be plotted and tabulated under various conditions and a mechanism supported by D studies to be proposed.

### Polymerisation of Butadiene by Rhodium Trichloride in Aqueous Medium - Effect of Electron Donors on Polymerisation

F. MIKES and J. KALAL, *Chem. Průmysl*, 1970, 20, (1), 17-20

The mechanism whereby aliphatic amines decrease the rate of butadiene polymerisation initiated by  $Rh Cl_3$  is discussed.

### Hydrogenation of Cycloalkenes Using Homogeneous Rhodium Complexes as Catalysts

A. S. HUSSEY and Y. TAKEUCHI, *J. org. Chem.*, 1970, 35, (3), 643-647

Initial rates of hydrogenation and pseudo-first-order rate constants are reported for several cycloalkenes in different solvent systems at  $25.0 \pm 0.1^\circ C$ ,  $p_{H_2} = 1$  atm with Rh complex catalysts. 3:1  $C_6H_6 : C_2H_5OH$  was the most effective solvent system. 1,2- and 1,3-dimethylcyclohexene are not hydrogenated with  $RhCl(Ph_3P)_3$ , nor is 1-methylcyclohexene with diphenylpiperidyl- or phenyldipiperidylphosphine complexes. Product ratios are discussed and the reaction mechanism is refined.

### Homogeneous Catalytic Hydrogenation and Exchange of Styrenes with Tris(triphenylphosphine)chlororhodium

G. V. SMITH and R. J. SHUFORD, *Tetrahedron Lett.*, 1970, (7), 525-527

Styrene hydrogenation and exchange reactions using this complex were compared with those on metal surfaces. Partial deuteration of styrene in  $\text{CHCl}_3$  yielded a novel product distribution. The mechanism of the exchange pattern with ethylbenzene is discussed and the presence of more than one catalyst system is proposed.

### Olefin Isomerisation over Tris(triphenylphosphine)chlororhodium

R. L. AUGUSTINE and J. F. VAN PEPPEN, *J. Chem. Soc., D, Chem. Commun.*, 1970, (8), 495-496

Olefin isomerisation over  $\text{Rh}(\text{Ph}_3\text{P})_3\text{Cl}$  is dependent on the presence of  $\text{O}_2$  in the system and on the solvent used.

### The Effect of Solvent on the Dissociation of Tris(triphenylphosphine)chlororhodium

*Ibid.*, 497

Dissociation of  $\text{Rh}(\text{Ph}_3\text{P})_3\text{Cl}$  to  $\text{Ph}_3\text{P}$  and  $\text{Rh}(\text{Ph}_3\text{P})_2\text{Cl}$  occurs quite readily in  $\text{C}_6\text{H}_6$  but is completely inhibited by the presence of even small amounts of  $\text{C}_2\text{H}_5\text{OH}$ .

### The Solvent Effect on the Oxidation of Tris(triphenylphosphine)chlororhodium

*Ibid.*, 497-498

$\text{Rh}(\text{Ph}_3\text{P})_3\text{Cl}$  oxidation products varied with the solvents used;  $\text{C}_6\text{H}_6$ ,  $\text{CH}_3\text{OH}$  and  $\text{C}_2\text{H}_5\text{OH}$ .

### Further Studies on Hydridocarbonyltris(triphenylphosphine)rhodium(I). Part I. Nature of Inactivation of Catalytic Reactions

M. YAGUPSKY, C. K. BROWN, G. YAGUPSKY and G. WILKINSON, *J. Chem. Soc., A, inorg. phys. theor.*, 1970, (6), 937-941

Hydrogenations and isomerisations of alkenes using  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$  are slowed down and are stopped eventually, especially in dilute solutions,

by decay of the catalyst to the complex  $[\text{Rh}(\text{CO})(\text{PPh}_3)_2]_2$ , which is inactive.

### Part II. Isomerisation of n-Pentenes and Hex-1-ene

M. YAGUPSKY and G. WILKINSON, *Ibid.*, 941-944

Rate studies on the homogeneous isomerisation of pent-1-ene using  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$  in  $\text{C}_6\text{H}_6$  solution showed that initially *cis*-pent-2-ene predominates over the *trans* isomer. *cis*→*trans* isomerisation was slower than conversion of pent-1-ene. Isomerisation to *cis*- and *trans*-pent-2-enes during hydrogenation of pent-1-ene at 1 atm, 27°C, occurs at about the same rate as hydrogenation.

### The Homogeneous Ruthenium-catalysed Reduction of Nitrobenzene

F. L'ÉPLATTENIER, P. MATTHYS and F. CALDERAZZO, *Inorg. Chem.*, 1970, 9, (2), 342-345

$\text{Ru}_3(\text{CO})_{12}$ ,  $\text{Ru}(\text{CO})_5$  and  $\text{Ru}(\text{acac})_3$  promote homogeneous reduction of  $\text{C}_6\text{H}_5\text{NO}_2$  to  $\text{C}_6\text{H}_5\text{NH}_2$  by CO and  $\text{H}_2$  in good yields and conversions. For  $\text{CO}:\text{H}_2 > 1$  the yield of by-product diphenylurea increases with the ratio  $\text{CO}:\text{H}_2$ . At high  $\text{CO}:\text{H}_2$  ratios the stoichiometry is probably  $\text{C}_6\text{H}_5\text{NO}_2 + 2\text{CO} + \text{H}_2 \rightarrow \text{C}_6\text{H}_5\text{NH}_2 + 2\text{CO}_2$ . The proposed mechanism includes a phenyl-nitrene intermediate stabilised by bonding to Ru in a binuclear complex. This undergoes hydrogenolysis to  $\text{C}_6\text{H}_5\text{NH}_2$  or CO insertion and hydrogenolysis to 2,2'-diphenylurea.  $\text{Fe}(\text{CO})_5$  is much less active than Ru for the reduction.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Palladium Silver Thick Film Conductors

*Electroplating Metal Finis.*, 1970 23, (3), 39

Two Pd-Ag ceramic conductive coatings for thick film microcircuits have been announced. The coatings, intended for the printing of high-quality, low-cost conductors, can be fired (700-1000°C) to give dense films with excellent adhesion, good solder leach resistance and high migration resistance.

## NEW PATENTS

### METALS AND ALLOYS

#### Alloy for Pen Points

W. C. HERAEUS G.m.b.H. U.S. Patent 3,480,429

An alloy suitable for use in the casting of pen points contains up to 50% of Os and/or Re, 30-45% Ir, 5-20% Ru, up to 25% of a noble metal, and up to 15% of base metal, e.g. Co.

### CHEMICAL COMPOUNDS

#### Organic Complexes of Platinum or Palladium

BRITISH PETROLEUM CO.

British Patent 1,181,485

Stable compounds of Pt or Pd are reacted with a tertiary phosphine and  $\text{H}_2$  in an inert organic solvent to produce organic complexes.