

# ABSTRACTS

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

## PROPERTIES

### The Gold-Nickel-Platinum System

S. M. CARMIO and J. L. MEIJERING, *Z. Metallkunde*, 1973, **64**, (3), 170-175

Isothermal studies between 812 and 1260°C of the Au-Ni-Pt system enabled the phase diagram to be defined. Solid miscibility in Au-Ni is increased by Pt, and in Au-Pt by Ni additions.

### High Pressure and High Field Properties of Nickel-Platinum Alloys near the Critical Concentration for Ferromagnetism

J. BEILLE, D. BLOCH and E. P. WOHLFARTH, *Phys. Lett., A*, 1973, **43A**, (3), 207-208

The static magnetic properties and their pressure derivatives were measured for 49.8-58.6% Pt-Ni. Results are in good agreement with the predictions of the homogeneous weak itinerant model and thus characterise these alloys as of the "Invar" type.

### Order Hardening in Equiatomic CuPt

R. MITCHELL, H. G. PARIS and B. G. LEFEVRE, *Metall. Trans.*, 1973, **4**, (3), 833-840

Structure studies of quenched and annealed CuPt showed a fine-domained mottled structure containing all four orientations for samples annealed for short times at 300 and 500°C. Continued annealing led to coarser domains with more ordering. Transformation to order and resultant changes of hardness depend on internal strains caused by cubic to rhombohedral distortion.

### Effects of Atomic Ordering on the Curie Temperature of Fe<sub>3</sub>Pt

T. MIZOGUCHI, M. AKIMITSU and S. CHIKAZUMI, *J. Phys. Soc. Japan*, 1973, **34**, (4), 932-933

The ferromagnetic Curie temperatures were measured for ordered and disordered phases of Fe<sub>1-x</sub>Pt<sub>x</sub>, where 0.25 ≤ x ≤ 0.30. The effect of atomic ordering on the Curie temperature is discussed in terms of a pair-interaction model. The Fe-Fe pair interaction is negative when only the nearest neighbour pair interactions are taken into account.

### The Chromium-Platinum Constitution Diagram

R. M. WATERSTRAT, *Metall. Trans.*, 1973, **4**, (6), 1585-1592

Metallographic, X-ray diffraction and electron microprobe studies of the Cr-Pt system indicated only one intermediate phase, which has Cr<sub>3</sub>Si(Al<sub>5</sub>)

structure. The f.c.c. Pt terminal solid solution extends to 71 at.% Cr at 1530°C with a congruent melting maximum at ~1790°C. Atomic ordering in this range begins at ~17 at.% Cr and there is continuous change from Cu<sub>3</sub>Au to CuAu-type structure as Cr content increases. Eutectics occur at 1530 ± 10°C and 1500 ± 10°C. A syntectic may occur at 1580 ± 10°C. Pt dissolves in the b.c.c. Cr terminal solid solution up to ~10 at.% Pt at 1500°C but solubility decreases rapidly at lower temperatures.

### Absorption of Hydrogen by Palladium/Rhodium Alloys and the Possible Existence of β-Phase Rhodium Hydride

T. C. WITHERSPOON, W. D. MCFALL and F. A. LEWIS, *Nature Phys. Sci.*, 1973, **242**, (116, Mar. 19), 44-45

Pressure-composition curves for the absorption of H<sub>2</sub> by Pd-Rh alloys suggest an endothermic value of 13000 cal/mol for the heat of formation of β-phase Rh hydride, which it has been suggested elsewhere may be formed at p<sub>H<sub>2</sub></sub> > 30,000 atm at 25°C.

### The Destruction of Short-range Order in Au-Pd Alloys by Cold Working

T. E. FINE and M. E. NICHOLSON, *Scripta Metall.*, 1973, **7**, (4), 383-386

The destruction of short-range order in Au-45 at.% Pd and Au-60 at.% Pd by cold working is non-linear in a manner not yet defined. There is also a limiting value of strain, small for the alloys in question, after which further straining causes negligible reduction in the short-range order.

### Diffusion of Hydrogen in Gold-Palladium Alloys

S. MAESTAS and T. B. FLANAGAN, *J. Phys. Chem.*, 1973, **77**, (6), 850-854

Diffusion constants for interstitial H<sub>2</sub> were determined for a series of randomly substituted f.c.c. Au-Pd alloys at small H<sub>2</sub> contents, where the dissolved gas behaves ideally. 20 at.% Au has little effect on the diffusion constant but for Au content greater than this, values of D decline logarithmically with Au content to D = 7.4 × 10<sup>-10</sup> cm<sup>2</sup>/sec for 55.7 at.% Au-Pd.

### Magnetic Susceptibility and Equilibrium Diagram of PdH<sub>n</sub>

H. FRIESKE and E. WICKE, *Ber. Bunsenges. Phys. Chem.*, 1973, **77**, (1), 48-52

To establish the limits n<sub>βmin</sub> and n<sub>αmax</sub> of the PdH<sub>n</sub> two-phase region, measurements of

magnetic susceptibility  $\chi$  as a function of  $H_2$  content in Pd were made at 20–300°C,  $p_{H_2}$  up to 140 atm for  $0 \leq n \leq 0.8$ , using Pd wire and foil.  $n_{\alpha_{max}}$  and  $n_{\beta_{min}}$  could then be determined by extrapolation. The critical point of the Pd-H system was then redetermined with good precision as  $T_c = 291 \pm 2^\circ\text{C}$ ,  $n_c = 0.250 \pm 0.005$  mol H/mol Pd,  $p_c = 19.7 \pm 0.2$  atm  $H_2$ . Studies using Pd black agreed for  $T_c$  and  $p_c$  but  $n_c$  was  $0.260 \pm 0.005$  mol H/mol Pd.

### Statistical Mechanics of a Three-component System: Pd-B-H

R. MEHLMANN, H. HUSEMANN and H. BRODOWSKY, *Ber. Bunsenges. Phys. Chem.*, 1973, 77, (1), 36–41  
Statistical mechanics of the Pd-H and Pd-B systems are extended to the Pd-B-H system. Absorption of  $H_2$  on Pd-B alloys can then be analysed in terms of the thermodynamics of the system and the energies between the atoms.

### The Eutectoid Region of the Ti-Pd System

J. C. WILLIAMS, H. I. AARONSON and B. S. HICKMAN, *Metall. Trans.*, 1973, 4, (4), 1181–1183  
Previous studies of the eutectoid region of the Ti-Pd system are in conflict. This study resolves the difficulty, establishes a new phase diagram of the region and points to transmission electron microscopy as the principal technique for phase diagram determination.

### The Chromium-Iridium Constitution Diagram

R. M. WATERSTRAT and R. C. MANUSZEWSKI, *J. Less-common Metals*, 1973, 32, (1), 79–89  
Metallographic, X-ray diffraction and electron microprobe studies of the Cr-Ir system show that it contains two intermediate phases, a  $\beta$  phase with  $Cr_2Si(Al_5)$ -type structure stable from ~73 to 82 at.% Cr, and a  $\epsilon$  phase with h.c.p. structure stable at 30–68 at.% Cr. The f.c.c. Ir terminal solid solution can dissolve ~28 at.% Cr and atomic ordering occurs in it from 16 at.% Cr to form a  $Cu_3Au$  structure up to the limit of solid solubility. Ir dissolves in the b.c.c. Cr terminal solid solution to ~12 at.% Ir at 1680°C but less at lower temperatures. Peritectic reactions occur at  $1750 \pm 10^\circ\text{C}$  and  $2200 \pm 50^\circ\text{C}$ . A eutectic occurs at  $1680 \pm 10^\circ\text{C}$ .

### Metastable Phases in Ti-Ru Alloys Rich in Titanium

L. N. GUSEVA, N. G. BORISKINA and L. K. DOLINSKAYA, *Izv. Akad. Nauk S.S.S.R., Metall.*, 1973, (3), 215–217  
Studies of the structure and hardness of cast and tempered  $\beta$ -phase alloys showed that  $\alpha'$ ,  $\alpha''$  and  $\omega$  metastable phases occur during tempering. Critical composition for  $\omega$ -phase formation is 3.8–8 at.% Ru, corresponding to an electron concentration of 4.16–4.32 electrons/atom. The ~9% difference in size between Ti and Ru

atoms appears to be critical for formation of the martensitic  $\alpha''$ -phase.

### Electrical Resistivity of Chromium-Ruthenium Alloys

T. F. DE YOUNG, S. ARAJS and E. E. ANDERSON, *J. Less-common Metals*, 1973, 32, (1), 165–169  
Resistivity-temperature curves for 6.6, 8.3, 10.1, 11.4, and 14.0 at.% Ru-Cr alloys possess large anomalies when antiferromagnetism appears. Néel temperatures  $T_N$  for these alloys and for other Cr-Ru alloys studied earlier were calculated and rise rapidly up to the 3 at.% Cr level, then plateau and then decrease with increasing Ru content. This behaviour and the resistivity-temperature curves are interpreted as due to the electron and hole Fermi surfaces of Cr and other changes as electron concentration increases.

### Phase Equilibria in the System Zirconium-Vanadium-Ruthenium

M. M. AKHVERDYAN, M. V. RAEVSKAYA, V. V. BURNASHEVA, E. I. GLADYSHEVSKII and E. M. SOKOLOVSKAYA, *Vest. Moskov. Univ., Ser. II, Khim.*, 1973, 14, (2), 182–186  
X-ray microscopic and hardness studies of the Zr-V-Ru system at 900–1500°C were carried out on annealed, quenched and as-cast alloys. An isothermal cross-section was obtained for the alloy annealed at 900°C.

### Reactions of Platinum Metals with Carbides of Groups IV and V of the Periodic System of the Elements during Sintering and Melting

E. RAUB and G. FALKENBURG, *Metall.*, 1973, 27, (7), 669–679  
Pt, Ru, Rh, and Ir were reacted with carbides of Ta, Ti and V. Structures of the materials produced by sintering and melting were tabulated.

## CHEMICAL COMPOUNDS

### The Stability of $K_2[Pt(CN)_4]Cl_{0.3} \cdot xH_2O$ in Wet and Dry Atmosphere

D. CAHEN, *Solid State Commun.*, 1973, 12, (11), 1091–1094  
The behaviour of the one-dimensional electrical conductor  $K_2[Pt(CN)_4]Cl_{0.3} \cdot xH_2O$  was studied at several temperatures in both wet and dry atmospheres. The material can be considered as a series of hydrates with  $x = 2.5$ –3. Effect of variation of  $x$  on physical properties is discussed.

### Reaction of $^{14}C$ -labelled Platinum Ethylenediamine Dichloride with Nucleic Acid Constituents

A. B. ROBINS, *Chem.-Biol. Interactions*, 1973, 6, (1), 35–45  
Reactions of  $Pt(en)Cl_2$  in 0.1 M  $NaClO_4$  with

adenine, guanine, cytosine, and their nucleosides and nucleotides were followed by radioactive labelling with  $^{14}\text{C}$ . Guanine derivatives reacted the most rapidly, notably guanosine. Probably more than one site on these compounds is available for reaction with  $\text{Pt}(\text{en})\text{Cl}_2$ .

#### Effect of *cis*-Dichlorodiammineplatinum(II) on Escherichia Coli B. Role of *fil*, *exr* and *hcr* Markers

J. DROBNIK, M. URBANOKOVA and A. KREKULOVA, *Mutat. Res.*, 1973, 17, (1), 13-20

Colony forming ability (C.F.A.) of Escherichia Coli B mutated at *fil*, *exr* and *hcr* loci was unaffected by *cis*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$  even at concentrations that reduce the C.F.A. of the parent strain by five orders of magnitude. Sensitivity to the Pt compound appears to depend on the pleiotypic response of the cells.

#### Suppression of Lymphocyte Blastogenesis in Man Following *cis*-Platinous Diamminodichloride Administration

A. KHAN and J. M. HILL, *Proc. Soc. Exp. Biol. Med.*, 1973, 142, (1), 324-326

Administration of 1-4 mg phytohemagglutinin/kg to subjects receiving *cis*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$  for various tumours significantly inhibited lymphocyte blastogenesis for 18-72 h. Single dose administration produced more inhibition than divided doses.

#### Thermal Expansion of Corundum Structure $\text{Rh}_2\text{O}_3$

L. J. ECKERT and R. C. BRADT, *Mater. Res. Bull.*, 1973, 8, (4), 375-378

X-ray diffraction measurements of the directional thermal expansion coefficients  $\alpha_a$  and  $\alpha_c$  of corundum structure  $\text{Rh}_2\text{O}_3$  at 0-850°C showed that it has lower thermal expansion and less anisotropy than  $\text{Al}_2\text{O}_3$ .  $\alpha_a = 5.350 \times 10^{-6} + 1.281 \times 10^{-9}\text{T} - 1.133 \times 10^{-14}\text{T}^2/^\circ\text{C}$  and  $\alpha_c = 5.246 \times 10^{-6} + 6.369 \times 10^{-9}\text{T} - 7.480 \times 10^{-14}\text{T}^2/^\circ\text{C}$ .

## ELECTROCHEMISTRY

#### Adsorptive and Catalytic Properties of Platinum Microcrystals Deposited on Inert Supports

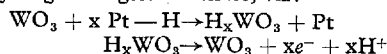
V. S. BAGOTSKII, L. S. KANEVSKII and V. S. PALANKER, *Electrochim. Acta*, 1973, 18, (7), 473-483

The electrochemical and catalytic properties of dispersed Pt catalysts on smooth, inert supports, i.e. Au or pyrographite, were studied.  $\text{H}_2$  adsorption on platinised pyrographite is markedly greater than that on plain pyrographite and the adsorption energy for deposited Pt differs from that of smooth Pt. The specific catalytic activity of deposited Pt in  $\text{H}_2$  evolution and ionisation, too, is greater than that of smooth Pt. This effect is most pronounced for small coverages of the support surface with Pt.

#### The Anodic Oxidation of Hydrogen on Platinised Tungsten Oxides. II. Mechanism of $\text{H}_2$ Oxidation on Platinised $\text{WO}_3$ Electrodes

B. S. HOBBS and A. C. C. TSEUNG, *J. Electrochem. Soc.*, 1973, 120, (6), 766-769

Electrochemical measurements of the anodic oxidation of  $\text{H}_2$  on a platinised  $\text{WO}_3$  electrode show that this support material takes an active part in the overall electrode reaction which proceeds by the formation and oxidation of hydrogen tungsten bronzes, viz:



## ELECTRODEPOSITION AND SURFACE COATINGS

#### Generative and Stabilising Processes in Tin-Palladium Sols and Palladium Sol Sensitisers

R. L. COHEN and K. W. WEST, *J. Electrochem. Soc.*, 1973, 120, (4), 502-508

Studies of sol systems produced by reduction of solvated Pd by  $\text{Sn}^{2+}$  show that the reduction is initiated by the formation of a polynuclear autoreductive Sn-Pd complex. Sol particles have Sn-Pd alloy cores with a stabilising layer of  $\text{Sn}^{2+}$  ions. The data are applied to commercial Pd sol systems for sensitising insulating surfaces for electroless plating. Other studies concerned the chemistry of the sensitising layer and the sol sedimentation rate.

#### Mechanism of Activation of Polymer Surfaces by Mixed Stannous Chloride/Palladium Chloride Catalysts

A. RANTELL and A. HOLTZMAN, *Trans. Inst. Metal Finish.*, 1973, 51, (2), 62-68

Studies by nephelometry and electron diffraction of the nature of  $\text{SnCl}_2$ -PdCl<sub>2</sub> catalysts used for activation of etched ABS surfaces before electroless Ni or Cu deposition showed no colloidal Pd. The active catalytic component is thought to be a complex Sn(II)-Pd(II) chloride. Activation involves hydrolysis of an adsorbed chloride complex within the ABS surface.  $\text{NH}_4\text{HF}_2$  accelerator presumably then causes a surface redox reaction to form active Pd nuclei. Immersion times in all pretreatment solutions, including rinses, directly affect the induction period.

## HETEROGENEOUS CATALYSIS

#### Catalyst Cuts Costs by Reducing Temperature for Incinerating Plant Odours

R. A. SEARLES, *Process Engng.*, 1973, (Feb), 100-102  
Honeycat ceramic honeycomb catalysts developed by Johnson Matthey allow incineration of unpleasant process odours to take place at much lower temperatures than with thermal incineration.

## Hydrogenation of Aromatic Hydrocarbons of 140–240°C Fractions on Platinum-Rhenium Catalyst

A. S. ZHURBA, YU. E. SMOL'NIK, KH. M. MINACHEV, M. A. RYASHENTSEVA, R. V. KATRUSH and A. D. MARTYNYUK, *Khim. Tekhnol., Topliv Masel*, 1973, (6), 7–9

Optimum conditions are given for hydrogenation of a wide range of straight-run fractions, evaporated at 140–204°C, over a Pt-Re catalyst. Analogous conversion on Pt/Al<sub>2</sub>O<sub>3</sub> occurs at 40 atm, 300°C.

## Application of Thermal Desorption Methods in Studies of Catalysis. I. Chemisorption of Carbon Monoxide on Platinum. II. The Oxidation of Carbon Monoxide on Platinum

W. L. WINTERBOTTOM, *Surface Sci.*, 1973, 36, (1), 195–204, 205–224

The desorption of CO from a polycrystalline Pt surface is characterised in terms of first order processes from essentially four surface states. A two-site adsorption process is proposed on the basis of a sequential adsorption pattern and distinguishable reactivity differences.

## Aromatisation of *n*-Nonane in the Presence of Platinum/Alumina Catalyst

V. F. IL'IN and YU. N. USOV, *Neftekhimiya*, 1973, 13, (3), 387–394

Acidic 0.5 wt. % Pt/Al<sub>2</sub>O<sub>3</sub> catalysed aromatisation of *n*-nonane at atmospheric pressure in a stream of H<sub>2</sub> at 310–490°C to form C<sub>9</sub> cyclic pentanes (*n*-butylcyclopentane, 1-methyl-2-*n*-propylcyclopentane, 1,2-diethylcyclopentane). These cyclanes are converted to aromatic C<sub>9</sub> hydrocarbons by dehydroisomerisation and C<sub>6</sub>-dehydrocyclisation. Isomerisation of C<sub>9</sub> alkylbenzenes in conditions for aromatisation of *n*-nonane does not play a significant role in forming isomeric aromatic hydrocarbons.

## Efficiency of Pt-Aluminosilicate Catalysts in H<sub>2</sub>O<sub>2</sub> Decomposition

T. G. MARTYNYUK, T. A. POSPELOVA, V. I. SHEKHOBALOVA and N. I. KOBOZEV, *Zh. Fiz. Khim.*, 1973, 47, (5), 1168–1171

Activity was related to Pt content for two series of Pt/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> produced by impregnation and by adsorption. Activity of Pt/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> was compared with that of Pt/CaY zeolite with the same Pt content. Activation energy of each was 10–11 kcal/mole.

## Effect of the State of Reduction on the Properties of Platinum Adsorption Catalysts

Z. V. LUK'YANOVA, V. I. SHEKHOBALOVA and N. I. KOBOZEV, *Zh. Fiz. Khim.*, 1973, 47, (4), 908–910  
0.7–70 wt. % Pt/aerosil catalysts were produced by low temperature reduction with NaBH<sub>4</sub> in solution. Tests of their activity for H<sub>2</sub>O<sub>2</sub> de-

composition were undertaken, and also measurements of specific activity and activation energy for catalysts reduced with NaBH<sub>4</sub> and with electrolytic H<sub>2</sub> at 300°C. H<sub>2</sub>O<sub>2</sub> decomposition is first order with respect to method of catalyst preparation, metal loading and H<sub>2</sub>O<sub>2</sub> concentration. Activity differs between the methods of reduction by 3–5 times.

## Rearrangement of Cyclic Amines Catalysed by Palladium

N. YOSHIMURA, I. MORITANI, T. SHIMAMURA and S.-I. MURAHASHI, *J. Chem. Soc., Chem. Commun.*, 1973, (9), 307–308

Pd suspended in pyrrolidone catalysed the rearrangement of cyclic amines to form *N*-substituted cyclic amines, and of heterocyclic amines to *N*-formyl cyclic amines.

## Catalytic Dehydrogenation of Coal: Part 7. The Effect of Some Catalyst Variables

L. REGGEL, I. WENDER and R. RAYMOND, *Fuel*, 1973, 52, (3), 162–163

The yield of H<sub>2</sub> during the catalytic dehydrogenation of vitrinite in the presence of phenanthridine as vehicle is most strongly influenced by which catalytic metal is chosen rather than its concentration or the nature of the support. Of a large variety of catalysts evaluated, Pd gave the highest yield.

## Arylation of Olefin with Iodobenzene Catalysed by Palladium

K. MORI, T. MIZOROKI and A. OZAKI, *Bull. Chem. Soc. Japan*, 1973, 46, (5), 1505–1508

Arylation of propylene, ethylene, styrene and methyl acrylate with iodobenzene is catalysed by metallic Pd in MeOH to give respectively methylstyrene, styrene, *z*-stilbene and methyl cinnamate. The yields and selectivities are increased significantly by the addition of excess potassium acetate as an acceptor of the hydriodic acid formed. The reaction is discussed in terms of the oxidative addition of iodobenzene to a Pd complex of low oxidation state.

## Relation of the Direction of Hydrogenolysis of Methylcyclopentane on Pd-Al<sub>2</sub>O<sub>3</sub> to the Electron Distribution in the Molecule

I. I. LEVITSKII, KH. M. MINACHEV and A. M. BOGANOV, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1973, (4), 762–767

Tests on the hydrogenolysis of methylcyclopentane showed that when the pressure was increased from 10 to 40–50 atm using Pt/Al<sub>2</sub>O<sub>3</sub> the ratios of *n*-C<sub>6</sub>H<sub>14</sub> to 2-methylpentane, of *n*-C<sub>6</sub>H<sub>14</sub> to 3-methylpentane, and of 3-methylpentane to 2-methylpentane in the products all increased but using Pd/Al<sub>2</sub>O<sub>3</sub> the ratios decreased. These results confirm that the process is connected with the charge on the C atom and the charge of the catalytic metal atom.

### Catalysis in Adsorbed Mixed Layers of d Elements Based on Platinum Metals with Variable Charging of the Surface

I. A. ZUBOVICH, *Zh. Fiz. Khim.*, 1973, **47**, (5), 1081-1094

Data on the activity of adsorption catalysts consisting of Pt and Pd with various additions of Ag, Cu, Re, Os, Ru, Ir, Rh, Pd in liquid phase hydrogenations, reductions, and H<sub>2</sub>O<sub>2</sub> decomposition, and also on the magnetic susceptibility of these systems enabled conclusions to be drawn on the possible formation of surface atomic structures and on electron-atom effects and microelectronics in heterogeneous catalysis.

### Liquid Phase Hydrogenation of Heptene-1 on Palladium-Rhodium Catalyst

L. A. SOKOLOVA, A. D. DEMBITSKII, N. M. POPOVA, D. V. SOKOL'SKII and M. I. GORYAEV, *Neftekhimiya*, 1973, **13**, (2), 174-179

Liquid phase hydrogenation of heptene-1 on 5% Pd-Rh/Al<sub>2</sub>O<sub>3</sub> is accompanied by double bond migration to form stereoisomers. The rate of H<sub>2</sub> absorption during this process is higher than on simple Pd or Rh catalysts and alters in direct relation to the content of adsorbed H<sub>2</sub>.

### Dealkylation of Xylenes by Reaction with Water Vapour on Rhodium Catalyst

G. L. RABINOVICH, L. M. TREISER, G. N. MASLYANSKII and A. A. TOKAREVA, *Neftekhimiya*, 1973, **13**, (3), 415-421

Xylenes are dealkylated over Rh at 400-480°C with H<sub>2</sub>O vapour to form C<sub>6</sub>H<sub>6</sub> and toluene. A secondary reaction is cleavage of the aromatic ring. Increasing the temperature during dealkylation of *o*-xylene does not affect the C<sub>6</sub>H<sub>6</sub>:toluene ratio but the ratio is increased during dealkylation of *m*-xylene.

### Hydrogenation of Ethylene and Benzene on Rhodium/Zelite Types A, X and Y

Z. V. GRYAZNOV, E. V. KOLODIEVA, V. P. PARANOSNIKOV, G. V. TSITSISHVILI and A. YU. KRUPENNIKOVA, *Neftekhimiya*, 1973, **13**, (3), 374-381

Zeolite supports for Rh are not inert, since the orders of activity are X>Y>A for C<sub>2</sub>H<sub>4</sub> hydrogenation and Y>X>A for C<sub>6</sub>H<sub>6</sub> hydrogenation both in pulsed and steady conditions. Adsorption of H<sub>2</sub>O affects the activity of the zeolites, depending on the sizes of the molecules to be reduced, the types of zeolite, the dislocations of the active centres in these structures, and the way the H<sub>2</sub>O is introduced into the zeolites.

### The Catalytic Reduction of Nitric Oxide over a Supported Ruthenium Catalyst

K. C. TAYLOR and R. L. KLIMISCH, *Abstr. Papers, 165th Natl. Mtg., Am. Chem. Soc.*, 1973, (Apr.), COLL 27

The reduction of NO by CO and H<sub>2</sub> over a sup-

ported Ru catalyst was studied using a feed stream resembling automobile exhaust gases. The effects of space velocity and reactant concentration on the NH<sub>3</sub>:N<sub>2</sub> product distribution and also the effect of these parameters on NO removal were investigated. The pertinent chemical reactions in this system and the limitations imposed by an exhaust gas feed stream are discussed.

## HOMOGENEOUS CATALYSIS

### Addition Reactions of Butadiene Catalysed by Palladium Complexes

J. TSUJI, *Accounts Chem. Res.*, 1973, **6**, (1), 8-15

Studies on oligomerisation and telomerisation of butadiene using Pd catalysts show that such reactions are unique and useful. Pd complexes catalyse cocyclisation of butadiene with heteropolar double bonds and telomerisation with nucleophiles. These reactions cannot be achieved with other transition metal complexes (76 references).

### Palladium(II)-catalysed Exchange and Isomerisation Reactions

P. M. HENRY, *Accounts Chem. Res.*, 1973, **6**, (1), 16-24

Expansion of homogeneous catalysis using Pd complexes has led to studies of reaction mechanisms, including those of vinyl ester exchange with radioactive chloride, allylic trifluoacetate exchange with chloride, vinyl chloride exchange with acetate, acid-catalysed allylic exchange, and *cis-trans* isomerisation (51 references).

### Isomerisation of Heptene-1 in the Presence of $\pi$ -Complexes of Palladium Chloride

YU. M. ZHOROV, G. V. DEMIDOVICH and G. M. PANCHENKOV, *Neftekhimiya*, 1973, **13**, (3), 395-400

Studies of homogeneous isomerisation of heptene-1 over PdCl<sub>2</sub> or  $\pi$ -complexes of PdCl<sub>2</sub> indicated double bond transfer to heptene-2 or -3 but no direct *cis-trans* isomerisation. The most active catalysts for this reaction are complexes containing olefin ligands. The formation of *trans* olefins during exchange of  $\pi$ -complex ligands includes transfer of H from the first to the third C atom.

### Palladium(II)-catalysed Exchange and Isomerisation Reactions. VIII. Isomerisation of Vinylic Halides in Acetic Acid Catalysed by Palladium(II) Chloride

P. M. HENRY, *J. Org. Chem.*, 1973, **38**, (6), 1140-1144

Pd(II)-catalysed isomerisation of *cis*- and *trans*-1-chloropropene obeys a three-term rate expression, the terms of which are analysed. Isomerisation of 1-cromopropene obeys mainly a two-term expression.

**Oxidation of Olefins by Palladium(II). VI. Ethylene Oxidation by Palladium(II) Acetate in Acetic Acid Promoted by Various Oxidants**  
P. M. HENRY, *J. Org. Chem.*, 1973, **38**, (9), 1681-1684

Like  $\text{CuCl}_2$  and  $\text{NO}_3^-$ , this study of Pd(II) salts in  $\text{CH}_3\text{COOH}$  as oxidants of  $\text{C}_2\text{H}_4$  showed that  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{NaNO}_3$ ,  $\text{CuBr}_2$ ,  $\text{MnO}_3$ ,  $\text{Pb}(\text{OAc})_4$ ,  $\text{Ti}(\text{OAc})_3$ ,  $\text{TiCl}_3$ , and  $\text{HAuCl}_4$  act as promoters to increase the oxidation rate and change the product from vinyl acetate to 1,2-disubstituted ethanes. Ethylidene diacetate was also formed when the three latter promoters were used. Other substances tested showed no promoting activity.

**Hydrogenation of Diene Hydrocarbons in the Presence of Chlorodimethylsulphoxide Complexes of Palladium**

L. KH. FREIDLIN, YU. A. KOPYTTSEV and N. M. NAZAROVA, *Neftekhimiya*, 1973, **13**, (3), 369-373

Chlorodimethylsulphoxide complexes of Pd are highly active in catalysing hydrogenation of dienes. The reaction is zero order with respect to dienes. It is selective, for no alkanes are formed during the addition of the first molecule of  $\text{H}_2$ . The hydrogenation forms non-equilibrium mixtures of olefins, predominantly *trans*-form  $\beta$ -isomers. Dienes are co-ordinated to Pd complexes during reduction mainly in the *trans* conformation.

**Investigation of the Homogeneous Reaction of Hydrogen Transfer from Pentanol-2 to Cyclohexanone, Catalysed by Tris(triphenylchlororhodium) in the Presence of Alkali**

L. KH. FREIDLIN, V. Z. SHARF, V. N. KRUTII and G. T. PROKOPENKO, *Kinet. Kataliz*, 1973, **14**, (3), 601-603

Studies of H transfer from pentanol-2 to cyclohexanone and of the hydrogenation of this by  $\text{H}_2$  in the presence of  $\text{RhCl}(\text{PPh}_3)_3$  catalyst and alkali show that the reaction proceeds through a number of stages.

**Activation of Hydrogen by Bridged Transition Metal Carboxylates. Rhodium(II)**

**Acetate Catalysed Hydrogenation of Olefins**  
B. C. Y. HUI, W. K. TEO and G. L. REMPEL, *Inorg. Chem.*, 1973, **12**, (4), 757-762

$\text{Rh}_2(\text{OOC.CH}_3)_4$  is an efficient and selective catalyst for hydrogenation of terminal olefins in various solvents, e.g. dec-1-ene in  $\text{N,N'$ -dimethylformamide. The initial step in the hydrogenation involves activation of H at only one metal centre in the dimeric catalyst. The H activation involving heterolytic splitting of  $\text{H}_2$  leads to formation of the intermediate  $\text{HRh}_2(\text{OOC.CH}_3)_3$ , which then reacts with the olefinic substrate. Olefin insertion into the metal-hydride bond followed by proton attack on the intermediate metal alkyl completes the catalytic cycle.

**Catalysis by Metal Complexes. IX. Catalytic Properties of Tris(diphenylphosphine)chlororhodium(I)**

P. SVOBODA, M. ČAPKA and J. HETFLJEŠ, *Coll. Czech. Chem. Commun.*, 1973, **38**, (4), 1235-1241

The catalytic activity of tris(diphenylphosphine)chlororhodium(I) in hydrosilylation, hydrogenation and hydroformylation was studied and compared with its analogue, tris(triphenylphosphine)chlororhodium(I). The diphenylphosphine complex is effective as a hydrosilylation catalyst but is a relatively poor hydrogenation catalyst; hydroformylation proceeds in its presence under comparatively mild conditions.

**In Situ High-pressure, High-temperature Spectrophotometric Studies of the Chloro-carbonylbis(triphenylphosphine)rhodium(I) Hydroformylation Catalyst Activated by Hydroperoxides**

H. B. TINKER and D. E. MORRIS, *J. Organometal. Chem.*, 1973, **52**, (2), C55-C75

The rate of hydroformylation of olefins catalysed by  $\text{RhClCO}(\text{Ph}_3\text{P})_2$  is accelerated by the addition of a small amount of cyclohexenylhydroperoxide which converts this mono-carbonyl complex into *cis*- $\text{RhCl}(\text{CO})_2\text{Ph}_3\text{P}$ , which is a highly active hydroformylation and isomerisation catalyst for olefins.

**Asymmetric Olefins Hydroformylation. III. Asymmetric Induction by Rhodium Complexes Using (—)-2,3-0-Isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane as Chiral Ligand**

C. SALOMON, G. CONSIGLIO, C. BOTTEGHI and P. PINO, *Chimia*, 1973, **27**, (4), 215-217

The asymmetric hydroformylation of aromatic olefins at atmospheric pressure and low temperature is promoted by  $\text{RhH}(\text{CO})(\text{Ph}_3\text{P})_3$  in the presence of (—)-2,3-0-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane. In the case of styrene asymmetric induction reaches 25%.

**Asymmetric Hydrosilation of Ketones Catalysed by a Chiral Cationic Rhodium Complex**

K. YAMAMOTO, T. HAYASHI and M. KUMADA, *J. Organometal. Chem.*, 1973, **54**, C45-C47

The catalytic behaviour of a cationic Rh complex, with an optically active phosphine as ligand, for the asymmetric hydrosilation of alkyl phenyl ketones is discussed.

**Homogeneous Dehydrogenation of Formic Acid by Complex Compounds of Monovalent Iridium**

E. N. YURCHENKO, *Kinet. Kataliz*, 1973, **14**, (2), 515-518

Studies of dehydrogenation of  $\text{HCOOH}$  in the

presence of  $\text{IrClCO}(\text{PPh}_3)_2$  at 1 atm, 20–50°C showed that the minimum permissible ratio of initial  $\text{K}_3\text{IrCl}_6$  to  $\text{PPh}_3$  in the complex is 1:7. The reaction is first order with respect to the initial complex and the acid. Dehydrogenation is preceded by formation of  $\text{IrCO}(\text{PPh}_3)_2\text{HCOO}$ .

### Hydrido Transition-metal Cluster Complexes

H. D. KAESZ, *Chem. Br.*, 1973, 9, (8), 344–352

These complexes, among which those of Ru and Os are important, may provide an important link between the study of soluble molecular complexes (homogeneous catalysis) and of solid state and surface phenomena (heterogeneous catalysis).

## FUEL CELLS

### Direct Biological Fuel Cell

J. F. HENRY and J. H. FISHMAN, *Extended Abstr.*, 143rd Mtg., *Electrochem. Soc.*, 1973, 73-1, (May), 723–724, abstr. 295

Au-Pd alloys are used for the electrodes of a direct fuel cell consuming  $\text{O}_2$  and fuels available in blood. Details of electrode construction and cell performance parameters are given.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Platinum-Rhenium-Tungsten Alloy Thin Film Resistors

C. Y. ANG, R. F. BAILEY and J. R. OGREN, *Extended Abstr.*, 143rd Mtg., *Electrochem. Soc.*, 1973, 73-1, 541–542, abstr. 221

Ternary alloy films were prepared by RF sputtering using a target 11% Re–20% W–Pt formed by powder metallurgy techniques. The sputtering procedure, composition analysis, thickness measurements, and determination of electrical resistivity as a function of film thickness and temperature are described.

### Stability of Thick-film Resistors under High Electromagnetic Stress

P. W. POLINSKI, *Solid State Technol.*, 1973, 16, (5), 31–35, 58

Tests on  $\text{RuO}_2$  crystal, Ru resinate and Pd-Ag

thick-film resistor compositions under high electromagnetic stress of several kV/in showed wide variations in conductivity. The conduction mechanism in the stable  $\text{RuO}_2$  composition for a total fired resistor thickness of 13–15  $\mu\text{m}$  forms very close to the  $\text{Al}_2\text{O}_3$  substrate in a microlayer a few  $\mu\text{m}$  thick. The conduction layer is thicker for lower resistivity compositions where the  $\text{RuO}_2$  content is higher but it is still close to the surface of the substrate. This formation is probably due to the dense  $\text{RuO}_2$  crystals settling out while the composition is held at the high peak firing temperature.

## TEMPERATURE MEASUREMENT

### Measurement of Temperature of the Glass Mass in a Furnace with a Cooled Metallic Cladding

A. G. GURKOV, V. I. POKOLENKO and V. N. RUSLOV, *Steklo Keram.*, 1973, (5), 11–12

Pt thermocouples with a cooled metallic cladding to protect them are used to compare the temperatures at various points in a furnace containing molten glass.

### The Departure of IPTS-68 from Thermodynamic Temperatures between 725°C and 1064.43°C

T. J. QUINN, T. R. D. CHANDLER and M. V. CHATTLE, *Metrologia*, 1973, 9, (1), 44–46

The departure of IPTS-68 from thermodynamic temperatures at 725–1064.43°C is discussed with particular reference to the Pt:13%Rh-Pt thermocouple.

### Contribution to the Study of the Effect of Pressure on the Platinum:Rhodium-Platinum Thermocouple

M. LALLEMAND, J. BRIELLES, D. VIDAL and P. MALBRUNOT, *J. Phys. D*, 1973, 6, (9), 1052–1057

Variations of the melting points of Au and Ag with pressure were measured with a Pt:10%Rh-Pt thermocouple under hydrostatic conditions. Results indicate a decrease of thermocouple e.m.f. with pressure, corresponding to  $0.5 \pm 0.2^\circ\text{C}/\text{kbar}$  between 960 and 1100°C.

## NEW PATENTS

### METALS AND ALLOYS

#### Hydrogen Diffusion Membranes

N. R. D. C. *U.S. Patent* 3,713,270

$\text{H}_2$  is separated from gas mixtures using membranes made from an alloy of Pd with lanthanides, (not La or Pr), e.g. 8.5%Y-Pd or 10%Ce-Pd.

#### Spinneret Alloy

COMPTOIR LYON-ALEMANT LOUYOT & CIE.

*French Patent* 2,133,178

Spinnerets for synthetic fibre production are made from an alloy of 80.5–90% Au, 10–19.5% Pt and 0–3% of at least one of Rh, Ir, Ru, Os and Re.