

# ABSTRACTS

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

### PROPERTIES

#### An X-ray Diffraction Study of Atomic Ordering in Platinum-rich Copper-Platinum Alloys

N.-C. WU, H. IWASAKI and S. OGAWA, *Trans. Japan Inst. Metals*, 1973, **14**, (4), 309-313

Ordering was studied in the Cu-Pt system at Pt concentrations of 48, 54, 61, 66 and 70 at.%. An ordered structure exists for the near-equiatomic composition, CuPt, and for the composition near CuPt<sub>3</sub>. There is, however, no evidence for the existence of an ordered structure for Cu<sub>3</sub>Pt<sub>5</sub>.

#### The Domains of Homogeneity of the Superconducting Phases in the Molybdenum-Platinum System

R. FLÜKIGER, K. YVON, C. SUSZ, R. ROGGEN, A. PAOLI and J. MÜLLER, *J. Less-common Metals*, 1973, **32**, (2), 207-225

Mo-Pt (up to 55 at. % Pt) was studied by metallography, X-ray diffractometry, hardness measurements, superconductivity and resistivity measurements for various thermal treatments. Results show that the phase diagram at high temperatures needs revision. In particular, the partially ordered  $\epsilon'$  hexagonal phase of the Ni<sub>3</sub>Sn (DO<sub>19</sub>)-type is responsible for the maximum superconducting transition temperatures.

#### The Superconductivity, Structure and Magnetic Susceptibility of Nb<sub>3</sub>Au<sub>x</sub>Pt<sub>(1-x)</sub> A-15 Type Phases

H. R. KHAN, E. RÖSCHEL and C. J. RAUB, *Z. Physik*, 1973, **262**, (4), 279-293

The superconducting transition temperature, lattice parameter and magnetic susceptibility of ternary Nb-Au-Pt alloys in the as-cast and annealed states were measured. Annealing reduced most of the alloys to A-15 structure as observed by X-ray diffraction, but metallographic microstructures of some of these alloys showed them to be still inhomogeneous, which affected the values of  $T_c$  and  $\chi$ . All the alloys are nearly paramagnetic and  $\chi$  varies with  $T_c$  in most cases.

#### The Debye Temperature of Pure Pd and Dilute Pd-Ni Alloys

J. E. VAN DAM and M. F. PIKART, *Phys. Lett. A*, 1973, **45**, (2), 147-148

The temperature dependence of the Debye temperature of dilute Pd-Ni alloys was studied. Results are compared with those for pure Pd and Pd-Cu and show that in pure Pd there is no

observable paramagnon contribution to the apparent lattice specific heat.

#### Effect of High Pressure on the Superconducting Transition Temperature of Pd-H

W. BUCKEL, A. EICHLER and B. STRITZKER, *Z. Physik*, 1973, **262**, (1), 1-4

Under hydrostatic pressure Pd-H exhibits a negative value of  $dT_c/dp$  comparable to that of non-transition superconductors. The isotope effect in Pd-H(D) is discussed in terms of a simple model which is in agreement with the observed pressure effect.

#### Kinetic and Magnetic Properties of Palladium-Iron Alloys. II. Temperature Dependence of Magnetisation and Thermal E.M.F.

L. I. ABRAMOVA, G. V. FEDOROV and N. V. VOLKENSHEIN, *Fiz. Metal. Metalloved.*, 1973, **36**, (3), 501-506

Measurements of the temperature dependence of magnetisation and of thermal e.m.f. of 0.5-99.5 at. % Fe-Pd alloys at 4.2-300 K enabled the value of magnetic saturation at 0 K to be used to calculate the mean magnetic moment and the moment on dissolved Fe atoms. Curie temperatures of dilute Fe-Pd alloys were determined by the thermodynamic potential method. An attempt was made to estimate the relative importance of the factors contributing to the thermal e.m.f.s. at various ranges of temperature.

#### On Some Phases in the Pd-Pb Mixture

M. ELLNER, T. GÖDECKE and K. SCHUBERT, *Z. Metallkunde*, 1973, **64**, (8), 566-568

Pd<sub>3</sub>Pb<sub>2</sub>, hitherto thought to be a homogeneous phase, is composed of four different phases, Pd<sub>3</sub>Pb<sub>3</sub>(h<sub>1</sub>), Pd<sub>3</sub>Pb<sub>3</sub>(h<sub>2</sub>), Pd<sub>3</sub>Pb<sub>3</sub> and Pd<sub>13</sub>Pb<sub>9</sub>. All phases are variants of the NiAs type. The structure of Pd<sub>3</sub>Pb<sub>3</sub>(h<sub>2</sub>) is confirmed; the structure of Pd<sub>3</sub>Pb<sub>3</sub> is isotypic to Ni<sub>5</sub>Ge<sub>3</sub>, and Pd<sub>13</sub>Pb<sub>9</sub> has a monoclinic cell.

#### The Diffusion of Hydrogen through Membranes of Palladium and Its Alloys with Silver

A. L. L'VOV, L. A. MALYSHEVA and O. I. PETROVSKAYA, *Zh. Fiz. Khim.*, 1973, **47**, (7), 1698-1701

Studies at 250-700°C and pressures up to 3 atm showed that the diffusion rate of H<sub>2</sub> through Pd and 25% Ag-Pd membranes is related to p<sub>H<sub>2</sub></sub> by Sivert's Law.

## Diffusion of Hydrogen from Converter Gases through Membranes of Palladium and Its Alloys

*Ibid.*, 1702-1706

Studies at 300-650°C and pressures of up to 3 atm showed that the rate of diffusion for H<sub>2</sub> from converter gases through Pd and 25%Ag-Pd membranes is related to p<sub>H<sub>2</sub></sub> by Sivert's Law. An approximate equation for the rate of diffusion of H<sub>2</sub> to the rate of feed of the gas mixture from the process is derived and shown experimentally for various process conditions.

## The Chromium-Rhodium Constitution Diagram

R. M. WATERSTRAT and R. C. MANUSZEWSKI, *J. Less-common Metals*, 1973, 32, (3), 331-343

The Cr-Rh system was studied over the entire composition range. Two intermediate phases exist in this system. The ε phase has an h.c.p. structure and is stable from 20 at.%Cr at 900°C to 68 at.% at 1475°C. The β phase has a Cr<sub>3</sub>Si (Al<sub>15</sub>) type structure and is stable from ~77-78 at.%Cr. The location of the f.c.c. (γ-Rh) to h.c.p. (ε phase) transition is strongly temperature dependent. Precipitation of a metastable h.c.p. structure occurs during rapid cooling of the b.c.c. (α-Cr) solid solution. A peritectic reaction, an eutectic reaction and a peritectoid reaction occur at 1700±10°C, 1475±10°C and 1265±12°C, respectively.

## Investigation of the Ternary System Iridium-Tantalum-Nickel

V. B. BERNARD, V. V. KUPRINA and V. V. BURNASHOVA, *Vest. Moskov. Univ., Ser. II, Khim.*, 1973, 14, (3), 350-353

The isothermal section of the Ir-Ta-Ni system at 950°C showed four intermetallic phases not previously noticed.

## CHEMICAL COMPOUNDS

### Radical Cation Formation during the Adsorption of Polycyclic Aromatic Hydrocarbons on Platinum Oxide

J. L. GARNETT, K. J. NICOL and A. RAINIS, *Aust. J. Chem.*, 1973, 26, (1), 221-224

Experimental conditions are reported for resolving the hyperfine splitting of e.p.r. spectra obtained from the interaction of polycyclic aromatic hydrocarbons with PtO<sub>2</sub>·2H<sub>2</sub>O. The adsorbed species are shown to be radical cations.

### New Compounds of Na<sub>x</sub>Pt<sub>3</sub>O<sub>4</sub> Structural Type

D. BERGNER and R. KOHLHAAS, *Z. Anorg. Allgem. Chem.*, 1973, 401, (1), 15-20

New members of the Na<sub>x</sub>Pt<sub>3</sub>O<sub>4</sub>-type platinates, Me<sub>x</sub>Pt<sub>3</sub>O<sub>4</sub>, where Me=Li, K, Ca, Ba, Co, Zn,

and Cd and 0 ≤ x ≤ 1 were prepared and are characterised by their lattice constants. Details of the thermal stability of both new and known platinates and palladates are given. Thermolysis of the palladates starts at 844-1020°C and of the platinates at 705-798°C. Decomposition gives either Pt metal and binary oxide or more stable palladates and platinates.

### Metallation of a Phenyl Group in a Platinum (II) Carbene Complex during Oxidation to Platinum(IV)

K. W. MUIR, R. WALKER, J. CHATT, R. L. RICHARDS and G. H. D. ROYSTON, *J. Organometal. Chem.*, 1973, 56, C30-C32

Reaction of Cl<sub>2</sub> with *cis*-[PtCl<sub>2</sub>{C(NHR)(NHR')}]PEt<sub>3</sub> and *trans*-[PtCl{C(NHR)(NHR')}](PEt<sub>3</sub>)<sub>2</sub> ClO<sub>4</sub> gives analogous Pt(IV) carbene complexes when R=R'=Me, but when R=Me or Et and R'=Ph, 2-metallation and 4-chlorine substitution of the phenyl group occurs as evidenced by the X-ray structure [PtCl<sub>2</sub>{C(ClC<sub>6</sub>H<sub>3</sub>NH)(NHMe)}(PEt<sub>3</sub>)<sub>2</sub>] ClO<sub>4</sub>.

### Dimeric Triphenylphosphine Complexes of Platinum(II)

F. R. HARTLEY and G. W. SEARLE, *Inorg. Chem.*, 1973, 12, (8), 1949-1951

The preparation of a new pale yellow isomer (probably *cis*-) of the bridged complex [(PPh<sub>3</sub>)<sub>2</sub>Pt<sub>2</sub>Cl<sub>4</sub>] and its reaction with *p*-toluidine and CO are described.

### Addition Reactions on Coordinated Olefinic Ligands. VII. Reaction between Amines and Pt(II) Olefin Complexes: Factors Affecting Reactivity and Stereochemistry

A. DE RENZI, G. PAIARO, A. PANUNZI and V. ROMANO, *Chim. e Ind.*, 1973, 55, (3), 248-251

The addition reaction between diethylamine and simple α-olefins coordinated in a variety of Pt(II) complexes was studied. Details of the reactivity of the unsaturated ligands towards the nucleophile and also data on the stereochemistry of the addition are given. The influence of relevant factors is discussed.

### Antitumour Action of Dichloro(4,5-dimethyl-*o*-phenylenediamine)platinum(II)

G. R. GALE, L. M. ATKINS, E. M. WALKER, A. B. SMITH and S. J. MEISCHEN, *Proc. Soc. Exp. Biol. Med.*, 1973, 142, (4), 1349-1354

Dichloro(4,5-dimethyl-*o*-phenylenediamine-N,N')platinum(II) is effective against the Ehrlich ascites tumour and L1210 leukemia in mice and increases survival times by 176% and 74% respectively. At ~4 × 10<sup>-5</sup> M concentration there is a 50% inhibition of DNA, RNA and protein synthesis in Ehrlich ascites tumour cells grown in vitro. Details for the synthesis of this compound is given.

**The Antitumour Agent  $cis\text{-Pt}(\text{NH}_3)_2\text{Cl}_2$ : Distribution Studies and Dose Calculations for  $^{193\text{m}}\text{Pt}$  and  $^{195\text{m}}\text{Pt}$**

R. C. LANGE, R. P. SPENCER and H. C. HARDER, *J. Nucl. Med.*, 1973, **14**, (4), 191-195

When  $cis\text{-Pt}(\text{NH}_3)_2\text{Cl}_2$  labelled with  $^{195}\text{Pt}$  was injected into mice bearing sarcoma 180, the tumour: blood ratio of radioactivity varied from 1:3 to 2:0 at 4 h-5 days after treatment. Details of organ distribution and of the metabolic pathways of this compound are discussed.

**$\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}(\text{H}_2\text{O})_{2.3}$  a Diamagnetic One-dimensional Metal?**

P. I. KUIJNDERSMA and G. A. SAWATZKY, *Solid State Commun.*, 1973, **13**, (1), 39-42

The magnetic susceptibilities of  $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}(\text{H}_2\text{O})_{2.3}$ ,  $\text{K}_2\text{Pt}(\text{CN})_4(\text{H}_2\text{O})_3$  and  $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_2$  were measured. Results show that any metallic type of contribution to the susceptibility of the first compound is at least an order of magnitude smaller than that expected from simple band theory or from an interrupted strand model.

**Optical Conductivity and Electron Interaction in the One-dimensional Metal  $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}\cdot 3\text{H}_2\text{O}$**

H. WAGNER, H. P. GESERICH, R. V. BALTZ and K. KROGMANN, *Solid State Commun.*, 1973, **13**, (6), 659-663

The optical conductivity of  $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}\cdot 3\text{H}_2\text{O}$  single crystals was studied for photon energies near the plasma edge. The imaginary part of the dielectric function is determined by elastic scattering of holes by the Coulomb potentials of randomly distributed Br ions and by inelastic scattering by excitation of plasmons.

**Optical Excitation of the Electronic Plasma Oscillation in the One-dimensional Conductor  $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.33}\cdot 3\text{H}_2\text{O}$**

P. BRÜESCH, *Solid State Commun.*, 1973, **13**, (1), 13-16

Reflectivity measurements with  $p$ -polarised light under non-normal incidence at a (001) surface of  $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.33}\cdot 3\text{H}_2\text{O}$  showed a resonance near the electronic plasma frequency. Results are discussed using the Fresnel formula for anisotropically absorbing crystals and classical dispersion theory for the description of the plasma oscillation.

**Reactions of Palladium(II) Compounds with Carbon Monoxide in Alcohol/Amine Systems: a New Route to Palladium(0) Carbonyl- and Carboalkoxy-palladium(II) Complexes**

M. HIDAI, M. KOKURA and Y. UCHIDA, *J. Organometal. Chem.*, 1973, **52**, (2), 431-435

$\text{Pd}(\text{o})$  carbonyl complexes,  $\text{Pd}(\text{CO})(\text{Ph}_3\text{P})_3$ ,  $\text{Pd}_3(\text{CO})_3(\text{Ph}_3\text{P})_3$  and  $\text{Pd}_3(\text{CO})_3(\text{Ph}_3\text{P})_4$  were pre-

pared by reacting  $(\text{Ph}_3\text{P})_2\text{PdCl}_2$  with CO at room temperature in MeOH/amine systems involving primary and secondary amines; these carbonyl complexes are interconvertible. The use of tertiary amines, however, gives selectively a carbomethoxy complex,  $(\text{Ph}_3\text{P})_2\text{PdCl}(\text{COOCH}_3)$ .

**Cyanoalkyl Complexes of Transition Metals. I. Preparation and Properties of Some Palladium Complexes**

K. SUZUKI and H. YAMAMOTO, *J. Organometal. Chem.*, 1973, **54**, 385-390

$\text{PdCl}(\text{CH}_2\text{CN})(\text{Ph}_3\text{P})_2$  was synthesised by reacting  $\text{Pd}(\text{Ph}_3\text{P})_4$  with  $\text{ClCH}_2\text{CN}$ . Compounds having the formula  $\text{PdX}(\text{CH}_2\text{CN})\text{L}$ , where  $\text{X}=\text{Cl}$  or Br and  $\text{L}=\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2$ ,  $\text{PPh}_2\text{CH}=\text{CHPPh}_2$ ,  $\text{PPh}_2\text{CH}_2\text{CH}_2\text{AsPh}_3$  or  $o$ -phenanthroline, were obtained by an exchange reaction of  $\text{PdCl}(\text{CH}_2\text{CN})(\text{Ph}_3\text{P})_2$  with the ligands. The structure of these complexes is discussed.

**The Carbonylation of  $\text{RuCl}_3\cdot x\text{H}_2\text{O}$  in Refluxing Ethanol**

M. L. BERCH and A. DAVISON, *J. Inorg. Nucl. Chem.*, 1973, **35**, (11), 3763-3767

The red solution formed by passing CO through a refluxing solution of  $\text{RuCl}_3\cdot x\text{H}_2\text{O}$  in EtOH is shown to contain  $\text{Ru}(\text{CO})_2\text{Cl}_2$ ,  $fac\text{-}[\text{Ru}(\text{CO})_3\text{Cl}_3]^-$  and  $\text{Ru}(\text{CO})\text{Cl}_2/[\text{Ru}(\text{CO})\text{Cl}_5]^{2-}$ . Ambiguities in the preparation and spectra of these and other Ru carbonyl halides are discussed.

**Infrared Spectroscopic Evidence for Dihydridotricarbonyl(triphenylphosphine)ruthenium**

R. WHYMAN, *J. Organometal. Chem.*, 1973, **56**, 339-343

The reactions of  $\text{Ru}(\text{CO})_4\text{PPh}_3$  and  $\text{Ru}(\text{CO})_5$  under pressures of  $\text{H}_2$  were studied using a high pressure spectrophotometric cell. Infrared spectral evidence was obtained for the formation of  $\text{H}_2\text{Ru}(\text{CO})_3\text{PPh}_3$  in reversible equilibrium with  $\text{Ru}(\text{CO})_4\text{PPh}_3$  and  $\text{H}_2$ . Reactions of  $\text{Ru}(\text{CO})_5$  with  $\text{H}_2$  at low temperatures affords  $\text{H}_2\text{Ru}(\text{CO})_4$  as the initial product. Above  $20^\circ\text{C}$  decomposition occurs resulting in the formation of polynuclear products.

**ELECTROCHEMISTRY**

**On the Influence of the Annealing Temperature and Heavy Current Treatments on the Porous Structure of Platinum Electrodes and on the Kinetics of the Oxygen Reaction at High Temperatures**

S. PIZZINI, M. BIANCHI, P. COLOMBO and S. TORCHIO, *J. Appl. Electrochem.*, 1973, **3**, (2), 153-159

The influence of high temperature annealing and anodic heavy current treatments of porous Pt electrodes was studied by scanning electron microscopy. Results are discussed on the basis

of the kinetic behaviour of the electrodes, whose structure and catalytic activity are affected by these treatments.

**Investigation of Adsorption Phenomena on Platinised Pt Electrodes by Tracer Methods. XII. Studies on the Adsorption of *n*-Propanol**  
G. HORÁNYI and M. NOVÁK, *Acta Chim. Acad. Sci. Hung.*, 1973, 75, (3), 271-279

The adsorption of *n*-propanol on a platinised Pt electrode was investigated by tracer methods. The process is an irreversible chemisorption that cannot be characterised by an equilibrium isotherm. The apparent concentration and potential dependences of adsorption are assumed to be due to certain oxidation-reduction reactions.

## LABORATORY APPARATUS AND TECHNIQUE

**A Thermistor Bimetal Thermocouple Hemisphere Electrode for Simultaneous Electrochemical/DTA Measurements**

B. B. GRAVES, *Rev. Sci. Instrum.*, 1973, 44, (5), 571-572

The construction of a thermistor bimetal thermocouple sensitive to thermal changes at the single electrode during scanning electrochemical experiments in liquid solutions is described. A Pt: 13% Rh-Pt thermocouple is incorporated in this device to permit caloric standardisation of differential thermal analysis thermogram peak areas from the known Peltier effect enthalpy change for passage of a known change across the couple.

## HETEROGENEOUS CATALYSIS

**Deactivation of Reforming Catalysts by the Growth of Platinum Crystals**

P. O. CONTIJOCH, R. M. MINERO and M. C. MALDONADO, *Rev. Inst. Mex. Petrol.*, 1973, 5, (1), 36-41

Crystal size data are used to make approximate determinations of the specific Pt areas in reforming catalysts and thus to predict the relative activity of the catalysts.

**The Reduction of Nitric Oxide with Carbon Monoxide and Hydrogen over Supported Noble Metal Catalysts**

T. P. KOBYLINSKI and B. W. TAYLOR, *Abstr. Papers*, 166th Natl. Mtg., Am. Chem. Soc., 1973, (Aug.), PETR 1

The reduction of NO with H<sub>2</sub>, CO and equimolar mixtures thereof was studied on Pt, Pd, Rh and Ru catalysts. Details of comparative catalytic activity for each reducing agent are given and a new reaction path, not involving the NH<sub>3</sub> decomposition step is proposed.

**Effect of the Pressure of Hydrogen on the Course of C<sub>5</sub>- and C<sub>6</sub>-Dehydrocyclisations of *n*-Octane over Platinised Carbon**

I. I. LEVITSKII, KH. M. MINACHEV and E. A. UDAL'TSOVA, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1973, (9), 2031-2035

During C<sub>5</sub>- and C<sub>6</sub>-dehydrocyclisations of *n*-C<sub>8</sub>H<sub>18</sub> at 375°C over 20% Pt/C, increasing p<sub>H<sub>2</sub></sub> causes more formation of 1,2-disubstituted rings, e.g. *o*-xylene and 1,2-methylethylcyclopentane. Reactions proceed via the general stage of formation of monoadsorbed complexes followed by subsequent conversion to the five- or six-membered rings.

**Isocyanate Intermediates in the Reaction NO + CO over a Pt/Al<sub>2</sub>O<sub>3</sub> Catalyst**

M. L. UNLAND, *J. Phys. Chem.*, 1973, 77, (16), 1952-1956

The intermediates formed by the interaction of NO and CO on a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst were studied by i.r. spectroscopy. Results show the existence of a Pt-NCO species and a (NCO)<sup>-</sup> anion, and provide a new mechanistic pathway and possible alternative to previous explanations of NH<sub>3</sub> formation in the catalytic treatment of automobile exhaust gases.

**A Study of Platinum-Polyamide Catalysts. Catalytic Behaviour in the Benzene Hydrogenation Reaction**

P. DINI, D. DONES, S. MONTELATICI and N. GIORDANO *J. Catalysis*, 1973, 30, (1), 1-12

Studies of C<sub>6</sub>H<sub>6</sub> hydrogenations over Pt/polyamides, Pt/polyacrylonitrile, Pt/molecular sieves, Pt/ion exchange resins, and Pt/Al<sub>2</sub>O<sub>3</sub> showed the effect of the supports on catalytic activity and selectivity. Only when Pt/polyamides are used is cyclohexene found as a reaction product. Various techniques showed that a bivalent Pt complex on the polyamide surface gives these catalysts their special selectivity.

**Kinetics of Dehydrogenation of Cyclohexane on Platinum/Alumina Catalyst in a Pulsed Regime**

YU. N. USOV, L. G. ZUBANOVA and N. I. KUVSHINOVA, *Neftekhimiya*, 1973, 13, (4), 504-508

Studies of the kinetics of cyclohexane dehydrogenation over Pt/Al<sub>2</sub>O<sub>3</sub> by the pulsed microcatalytic method in a stream of H<sub>2</sub> and He enabled the kinetic constants to be determined. The reaction products in these conditions inhibit the reaction.

**Formation of Coke in Conditions of Reforming Aromatic and Naphthenic Hydrocarbons on Platinum/Alumina Catalyst**

YU. V. FOMICHEV, T. V. KURCHATKINA, M. E. LEVINTER and E. F. BOL'SHAKOV, *Neftekhimiya*, 1973, 13, (4), 540-545

The yield of coke during aromatisation of hydro-

carbons increases in the order benzene < toluene < *m*-xylene < *n*-xylene < *o*-xylene < ethylbenzene < tributylbenzene < isopropylbenzene. Coking of the catalyst during dehydrogenation of naphthenic hydrocarbons leads to reduced selectivity of aromatisation because of a strengthening of the role of acid centres and to a weakening of the dehydrogenating action of the catalyst.

#### Hydrogenation of Aromatic Hydrocarbons of Jet Fuel Fractions on Platinum Catalysts

A. S. ZHURBA, YU. E. SMOL'NIK, KH. M. MINACHEV, M. A. RYASHENTSEVA, N. I. VYKHRESTYUK, E. K. BRYANSKAYA and A. D. MARTINYUK, *Neftekhimiya*, 1973, **13**, (4), 499-503

Studies of the hydrogenation of aromatic hydrocarbons in jet fuel fractions over Pt/Al<sub>2</sub>O<sub>3</sub> and Pt-Re/Al<sub>2</sub>O<sub>3</sub> show that there is a more thorough and selective conversion on Pt-Re/Al<sub>2</sub>O<sub>3</sub>. In contrast to Pt/Al<sub>2</sub>O<sub>3</sub>, conversion over Pt-Re/Al<sub>2</sub>O<sub>3</sub> of a series of aromatic hydrocarbons increases as the molecular weight rises.

#### Isomerisation of *n*-Hexane and Dehydrogenation of Cyclohexane in the Presence of Catalysts Containing Platinum on Zeolites, Suspended in Aluminium Oxide

N. S. KOZLOV, I. I. URBANOVICH, V. S. KOMAROV and M. V. ZARETSKII, *Neftekhimiya*, 1973, **13**, (4), 487-491

Studies of isomerisation of *n*-C<sub>6</sub>H<sub>14</sub> and of dehydrogenation of cyclohexane on Pt supported on zeolites in an Al<sub>2</sub>O<sub>3</sub> matrix show that these catalysts possess the isomerising capacity of Pt/zeolites and surpass Pt/Al<sub>2</sub>O<sub>3</sub> in this respect. 20% HY zeolite addition to Pt/Al<sub>2</sub>O<sub>3</sub> reforming catalyst raises the temperature at which Pt crystallises.

#### The Effect of Binding Substances on the Hydrocracking Activity of Platinum-Zeolite Catalysts

A. M. TSYBULEVSKII, I. S. VOL'FSON, B. A. LIPKIND, T. R. BANKOVSKAYA, R. A. SERDYUK, L. N. GIMADEEV, A. T. SLEPNEVA and E. N. BEREZOVSKAYA, *Khim. Tekhnol., Topliv Masel*, 1973, (7), 3-6

Pt/zeolite catalysts have greater hydrocracking activity if the zeolite has a high silica content. The best catalytic, diffusion and mechanical properties are possessed by such zeolites with kaolinite as a binder.

#### 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

When vitrinite is catalytically dehydrogenated in the presence of phenanthrene as vehicle, the H<sub>2</sub> yield is not greatly influenced by the catalyst support or concentration but by the metal used. The highest H<sub>2</sub> yield is achieved by Pd.

#### Platinum and Palladium Catalysed Hydrogenation, Racemisation, Exchange and Double Bond Migration in Substituted Cyclohexenes

G. V. SMITH, J. A. ROTH, D. S. DESAI and J. L. KOSCO, *J. Catalysis*, 1973, **30**, (1), 79-85

Partial deuteration of methyl-substituted cyclohexenes showed considerable exchange and double bond migration over 5% Pd/C but over 5% Pt/C hardly any double bond migration occurred in the cyclohexene ring although up to 60% of the recovered molecules were on the surface and 25% of them exchanged at least one H for D.

#### Hydrogen-Oxygen Titration Method for the Measurement of Supported Palladium Surface Areas

J. E. BENSON, H. S. HWANG and M. BOUDART, *J. Catalysis*, 1973, **30**, (1), 146-153

Pd dispersion on 5% Pd/Al<sub>2</sub>O<sub>3</sub>, measured by titration by H<sub>2</sub> or D<sub>2</sub> at 100°C of O<sub>2</sub> preadsorbed on the catalyst, agrees with results of other methods and has distinct advantages over them because of the method's sensitivity and its suitability for use where the catalyst has been exposed to the air.

#### Dispersion and Activity of Palladium in Catalysts for Hydrogenation of Phenol

G. D. LYUBARSKII, N. E. BUYANOVA, I. D. RATNER and M. M. STRELETS, *Kinet. Kataliz.*, 1973, **14**, (4), 1020-1023

The dispersion of Pd in 0.25-2.0% Pd/γ-Al<sub>2</sub>O<sub>3</sub> during hydrogenation of C<sub>6</sub>H<sub>5</sub>OH was determined by electron microscopy and by O<sub>2</sub> chemisorption studies. The specific activity of Pd on this support remains constant while the kinetics of the reaction are steady. Selectivity and efficiency of the catalyst are related to the thickness of the active Pd layer on the catalyst particles.

#### Heterogeneously Catalysed Vapour-phase Oxidation of Ethylene to Acetaldehyde

A. B. EVNIN, J. A. RABO and P. H. KASAI, *J. Catalysis*, 1973, **30**, (1), 109-117

A heterogeneous catalyst for vapour-phase oxidation of C<sub>2</sub>H<sub>4</sub> to CH<sub>3</sub>CHO consists of Pd-doped V<sub>2</sub>O<sub>5</sub> with a third component such as Ti, Ru, Pt, or Ir. The Pd ions play an important part in the redox mechanism. This catalyst operates well at 110-175°C, 1-30 atm with high space-time yields.

#### Supported Metals. Preparation of Palladium on Silica, Alumina, Magnesia, and Aluminium Silicate

R. GOMEZ and F. FIGUERAS, *Rev. Inst. Mex. Petrol.*, 1973, **5**, (1), 47-51

Catalysts prepared by the impregnation of Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, MgO and silico-aluminas with either

PdCl<sub>2</sub> in aqueous HCl or with Pd(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> in 10N NH<sub>4</sub>OH showed almost total fixing of Pd and significant chlorination by the HCl medium. Alternate preparation by ion exchange takes place by a cationic or anionic mechanism with Pd(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> or K<sub>2</sub>PdCl<sub>4</sub>, respectively. The amount of Pd retained is dependent on the support and on the salt used for ion exchange.

### Heterogeneous Selective Catalysis of the Hydrogenation of Olefins by Polymeric Palladium(II) and Platinum(II) Complexes

H. BRUNER and J. C. BAILLAR, *Inorg. Chem.*, 1973, **12**, (7), 1465-1470

The preparation of a polymeric diphenylbenzylphosphine ligand and of its Pd(II) and Pt(II) dichloride complexes is described. The effectiveness of these complexes as olefin hydrogenation catalysts is discussed.

### Dehydrocyclisation of 2-*n*-Butylnaphthalene in the Presence of Iridium/Alumina Catalysts

G. A. SHEVTSOVA, L. A. ERIVANSKAYA and A. F. PLATE, *Neftekhimiya*, 1973, **13**, (4), 509-513

Studies of 2-*n*-butylnaphthalene conversion over 0.5 wt.% Ir/Al<sub>2</sub>O<sub>3</sub> at 370-490°C, space velocity 0.8-0.2 h<sup>-1</sup>, showed that C<sub>6</sub>- and C<sub>5</sub>-dehydrocyclisation at the α- and β-C atoms of naphthalene depends on the temperature; at 370-410°C cyclisation at the β-C atom predominates but at 450-490°C cyclisation at the α-C atom predominates.

## HOMOGENEOUS CATALYSIS

### Palladium(II) Acetate Catalysed Reactions of Olefins in Acetic Acid

P. M. HENRY and R. N. PANDEY, *Abstr. Papers*, 166th Natl. Mtg., Am. Chem. Soc., 1973, (Aug.), INDE 20

The results of several investigations of Pd(II) acetate catalysed reactions are summarised. These include vinyl and allylic ester exchanges with solvent to give vinyl and allylic acetates and also some olefin oxidation reactions.

### Palladium(II) Catalysed Aromatic Acetoxylation. II. Nuclear Acetoxylation of Aromatic Compounds: A Reversal of the Usual Isomer Distribution Pattern in Aromatic Substitution

L. EBERSON and L. GOMEZ-GONZALEZ, *Acta Chem. Scand.*, 1973, **27**, (4), 1249-1254

The reaction between monosubstituted aromatics and Pd(II) acetate in CH<sub>3</sub>COOH in an O<sub>2</sub> atmosphere was studied. The monoacetoxylation products from compounds containing *o*, *p*-directing substituents consist of predominantly *meta* isomer, whereas one compound with a *meta*-orienting substituent gives mainly *o*, *p*-acetoxylation. Isomer distributions are thus reversed

with respect to ordinary electrophilic aromatic substitutions. Polymethyl-substituted benzenes give side chain acetoxylation products.

### Noble Metal Catalysis. II. Hydratocarbonylation Reaction of Olefins with Carbon Monoxide to Give Saturated Acids

D. M. FENTON, *J. Org. Chem.*, 1973, **38**, (18), 3192-3198

The hydratocarbonylation reaction of olefins with CO to give saturated acids was studied in the presence of a catalyst - probably a zerovalent Pd-phosphine complex. The reaction rate is dependent on olefin concentration and CO pressure and reaches a maximum with a H<sub>2</sub>O concentration of 5-10%. The catalyst system undergoes a number of changes between the zero and plus two valence states, some of which probably involve the carbon moieties attached to the phosphine ligand.

### Isomerisation and Hydrogenation of Isopentenes in the Presence of Chlorodimethylsulphoxide Complexes of Palladium

L. KH. FREIDLIN, YU. A. KOPYTSEV and N. M. NAZAROVA, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1973, (8), 1903-1904

Chlorodimethylsulphoxide complexes of Pd catalyse the hydrogenation and isomerisation of 3-methylbutene-1 to form a mixture of isopentenes. Isomerisation of 3-methylbutene-1 takes place with the aid of hydride complexes according to the π-allyl mechanism. 2-Methylbutene-1 is formed directly from 3-methylbutene-1 rather than by successive transfers of the C=C bond.

### Properties of Sodium Bis-(2-methoxyethoxy) aluminium Hydride. XIV. Dehalogenation in the Presence of Palladium Complexes

E. ŠIMŮNEK and M. KRAUS, *Coll. Cz. Chem. Commun.*, 1973, **38**, (6), 1786-1790

Dehalogenation of aliphatic and aromatic halogeno derivatives with NaAlH<sub>2</sub>(OC<sub>2</sub>H<sub>4</sub>OCH<sub>3</sub>)<sub>2</sub> is accelerated by catalytic amounts of Pd complexes, the strongest effect being in the aromatic series where even fluorobenzene is reduced. The effects of the amount of catalyst and nature of the halogen are discussed.

### Catalytic Codimerisation of Styrene with Lower Olefins by Rhodium and Ruthenium Catalysts

H. UMEZAKI, Y. FUJIWARA, K. SAWARA and S. TERANISHI, *Bull. Chem. Soc. Japan*, 1973, **46**, (7), 2230-2231

The codimerisation reaction of styrene with lower olefins such as ethylene, propylene or 1-butene were studied in the presence of a number of Rh(III) and Ru(III) compounds. Details of reaction products and comparative yields are given.

### Rhodium Complexes of Chiral Phosphines as Catalysts for Asymmetric Homogeneous Hydrogenation

J. D. MORRISON, *Strem Chemiker*, 1973, 1, (1), 3-7

The use of a series of soluble Rh complexes, prepared from chiral tertiary phosphines, as catalysts for asymmetric homogeneous hydrogenation is discussed. These catalysts show nearly complete, enzyme-like stereoselectivity and represent a vast improvement in performance over that of simpler chiral-supported heterogeneous catalysts.

### Hydrogenation of Tris(triphenylphosphine)-chlororhodium(I)

J. HALPERN and C. S. WONG, *J. Chem. Soc., Chem. Commun.*, 1973, (17), 629-630

The reactivities of  $\text{RhCl}(\text{PPh}_3)_3$ ,  $\text{RhCl}(\text{PPh}_3)_2$  and  $\text{Rh}_2\text{Cl}_2(\text{PPh}_3)_4$  towards  $\text{H}_2$ , and the contributions of each of these species to the overall rate of hydrogenation of  $\text{RhCl}(\text{PPh}_3)_3$  in solution were determined.  $\text{RhCl}(\text{PPh}_3)_2$  is at least  $10^4$  times as reactive as the other two species.

### Hydrogenation and Dehydrogenation of Chlorotris(triphenylphosphine)rhodium(I)

G. G. STRATHDEE and R. M. GIVEN, *J. Catalysis*, 1973, 30, (1), 30-39

The amount of  $\text{H}_2$  absorbed per mole of  $\text{RhCl}(\text{PPh}_3)_3$  differs from that recovered by an inert gas purging technique when using  $\text{C}_6\text{H}_6$ ,  $\text{CH}_2\text{Cl}_2$  and 50%  $\text{C}_2\text{H}_5\text{OH}-\text{CHCl}_3$  solutions. In the last case the reversibly bound H:Rh ratio is only  $\sim 0.3$  at 298K because  $\text{RhHCl}(\text{PPh}_3)_2$  has been formed, whereas in  $\text{C}_6\text{H}_6$  the ratio is 0.85 and in  $\text{CH}_2\text{Cl}_2$  it is 0.66.

## NEW PATENTS

### METALS AND ALLOYS

#### Novel Platinum-Rhodium-Tungsten Alloy

UNITED STATES ATOMIC ENERGY COMMISSION

U.S. Patent 3,737,309

A new alloy composition comprising 25-30% Rh, 6-10% W with the remainder Pt, is useful for encapsulating radioisotope fuels. It has a melting point of 1980-2050°C.

#### Wrought Dispersion Strengthened Metals by Powder Metallurgy

INTERNATIONAL NICKEL CO. INC.

U.S. Patent 3,738,817

Powder metallurgy is used to produce Pt-based alloys by dispersion hardening with uniform distribution of the dispersed agent transversely and longitudinally.

### Homogeneous Olefin Hydrogenation Catalysed by Dichlorodicarbonyl-bis(triphenylphosphine)ruthenium(II)

D. R. FAHEY, *J. Org. Chem.*, 1973, 38, (19), 3343-3348

The relative hydrogenation rates for a variety of alkenes and alkadienes catalysed by  $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$  were measured in the presence of added  $\text{PPh}_3$ . Reaction rates and the means of obtaining selective hydrogenation are discussed.

## GLASS TECHNOLOGY

### Observation of Contact Phenomena in Glass/Metal Systems

G. J. COPLEY, A. D. RIVERS and R. SMITH, *J. Mater. Sci.*, 1973, 8, (7), 1049-1051

A study of the glass droplets found near the wetting edge of glass sessile drops on Pt has clarified the deposition process and the influence of the Pt grain structure on their nucleation and growth. The mode of grain boundary movement during grain growth is discussed.

## TEMPERATURE MEASUREMENT

### A Reciprocal Kelvin Temperature Sensor

L. FOWLER and W. N. TRUMP, *Rev. Sci. Instrum.*, 1973, 44, (9), 1333-1334

A simple bridge circuit using a Pt resistance thermometer is described which generates a signal proportional to  $1/T$  with an error  $< 0.1\%$  over a wide range. The superiority of Pt over other materials is discussed.

### Metal Atomisation

JOHNSON, MATTHEY & CO. LTD.

French Appl. 2,148,349

Metal articles are produced by arc, flame or plasma spraying metal droplets at a cold target to form a coherent layer of individual particles which are then mechanically worked to a mass. The metal is particularly a Pt-group metal or alloy, e.g. an alloy of 49% Pt, 50% Au and 1% Rh.

### Alloy for Metering Instruments

F.A. CARL HAAS

German Offen. 2,206,397

Suspension strips for meters are made from Pd and/or Pt containing small amounts of at least one Group III-VI element to increase corrosion resistance and deformability. Au, Ag and Cu may also be present.