

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

The Heat of Adsorption of Hydrogen on Platinum

P. R. NORTON and P. J. RICHARDS, *Surface Sci.*, 1974, **44**, (1), 129-140

UHV adiabatic calorimetric studies of the heat of adsorption (q) of H on clean polycrystalline Pt determined as a function of the coverage (θ) and temperature showed that adsorption at 273 K resulted in a stepped shape $q-\theta$ curve with $q(\theta=0)=24.7$ kcal/mole. At 77 K the form of the curve depends on the temperature of pre-adsorption.

Temperature-dependence of Resistivity of PtCr Alloys

R. M. ROSHKO and G. WILLIAMS, *Phys. Rev. B*, 1974, **9**, (11), 4945-4953

Studies of the electrical resistivity of 5-12% Cr-Pt alloys at 1.4-300 K showed that the spin-fluctuation temperature increased from 52.5 to 85 K as Cr concentration increased from 5 to 12 at.%. No magnetic ordering occurs above 1.4 K for concentration < 12 at.%; a rough calculation is performed which qualitatively accounts for the decreasing magnetic-ordering temperature across the series AuCr, PdCr and PtCr.

Magnetic Structure of Ordered Iron-Platinum Alloys

A. Z. MEN'SHIKOV, YU. A. DOROFEEV, V. A. KAZANTSEV and S. K. SIDOROV, *Fiz. Metal. Metalloved.*, 1974, **38**, (3), 505-518

Elastic scattering of neutrons and magnetic measurements on 10-75 at.% Fe-Pt alloys revealed five magnetic structures corresponding to Pt_3Fe , $Pt_{2.75}Fe_{1.25}$, $Pt_{2.5}Fe_{1.5}$, $PtFe$, and Fe_3Pt . Their magnetic properties vary from antiferromagnetic ordering in Pt_3Fe and $Pt_{2.75}Fe_{1.25}$ to ferromagnetic in $Pt_{2.5}Fe_{1.5}$ and Fe_3Pt . $FePt$ is believed to possess uncompensated antiferromagnetism, i.e. ferrimagnetism. Experimental and theoretical values are in best agreement for atomic moments of Fe (3.0-2.75) μ_B and Pt (0.2-0.3) μ_B .

The Reversible Martensite Transformation in Iron-Platinum Alloys near Fe_3Pt

S. KAJIWARA and W. S. OWEN, *Metall. Trans.*, 1974, **5**, (9), 2047-2061

A series of 25-27 at.% Pt-Fe alloys with ordering of the γ phase varying from substantial disorder to nearly complete order were thermally cycled at 25-196°C. The kinetics of the $\gamma \rightleftharpoons \alpha$ trans-

formations, the hysteresis revealed by electrical resistance/temperature plots, the thermoelastic growth and the reappearance of an identical microstructure after thermal cycling were studied as a function of the ordering of the γ -phase.

Localised Enhancement Effects in Pd-Ag Alloys

A. P. MURANI, *Phys. Rev. Lett.*, 1974, **33**, (2), 91-94
Low-temperature electrical resistivities of Pd-Ag alloys show a positive T^2 temperature dependence in the concentration range above 60 at.% Ag. This behaviour supplements the well-known resistivity minima observed in alloys with lower concentrations of Ag, and strongly favours the model of scattering from localised exchange-enhanced Pd d states, as against $s \rightarrow d$ scattering in the rigid- or collective-band description of the alloys.

Surface Area Effects on the Sorption of Hydrogen by Palladium

M. J. B. EVANS, *Can. J. Chem.*, 1974, **52**, (7), 1200-1205

Pressure-composition isotherms for dilute solutions of H_2 in Pd were measured at 100-240°C and at up to 1000 Torr. For Pd foil the isotherms are consistent with data at lower temperatures, and with existing theoretical isotherms. With samples of appreciable surface area a higher sorptive capacity is found which may be due to the formation of a layer of adsorbed H_2 on the metal surface; appropriate correction may be made for this. The variation of partial molar enthalpy of adsorbed H_2 with H_2 -content is also affected by this surface phenomenon.

Electrical Resistivity of Some Palladium-Silver Alloys Containing Hydrogen at 4.2 K

R. J. SMITH and D. A. OTTERSON, *NASA Tech. Note D-7672*, 1974, (May), 11 pp.

The resistivities of the alloys of 50-90% Pd and 50-10% Ag measured as a function of absorbed H at 4.2 K showed minimum and maximum values, except for 10% Ag-Pd, which had only a maximum, and 50% Ag-Pd with only a minimum.

Effect of Pressure on the Curie Temperatures of PdFe, PdCo, PtFe and PtCo Alloys

J. S. MEIER, C. W. CHRISTOE and G. WORTMANN, *Solid State Commun.*, 1974, **15**, (3), 485-488

The Curie temperatures of PdFe, PdCo, PtFe, and PtCo alloys with Fe or Co concentration of 1-10 at.% have been measured by thermal

scanning of the ^{57}Fe Mössbauer resonance under pressures up to 170 kbar. The data are compared with models, which relate the variation of T_c under pressure to changes in the impurity spin-conduction electron coupling parameter J_i and to changes of the pure host susceptibility χ_H . The differences between the experimental data and these models are discussed.

High Pressure Magnetic Behaviour of Low Nickel Content Pd-Ni Alloys

J. BEILLE, *Phys. Lett. A*, 1974, **49**, (1), 63-64

The magnetic properties of disordered Pd-Ni alloys, with low Ni content were studied at high magnetic fields and at high pressures. The variation of the saturation magnetisation and Curie temperature with the concentration and pressure are described.

Defects in Glassy Pd-Si Alloys

J. LOGAN, *Scripta Metal.*, 1974, **8**, (6), 727-732

X-ray diffraction and density studies on as-quenched and rolled $\text{Pd}_{80}\text{Si}_{20}$ showed that X-ray diffracted intensities were identical for both as-quenched and rolled foils but the density of the as-quenched foils is $\sim 5\%$ while the rolled foils vary by $\sim 0.3\%$. The increase in the density upon rolling is 0.5-5.8%.

The Glass Transition Temperature in Glassy Alloys: Effect of Atomic Sizes and the Heats of Mixing

H. S. CHEN, *Acta Metall.*, 1974, **22**, (7), 897-900

The glass transition temperature T_g of glassy systems $(\text{Pd}_{1-x}\text{M}_x)_{0.835}\text{Si}_{0.165}$ for $\text{M}=\text{Cu}$, Ag , Au , Rh , Ni , Co and Fe and $(\text{Pd}_{1-x}\text{N}_x)_{0.80}\text{P}_{0.20}$ for $\text{N}=\text{Ni}$, Co and Fe was studied. The lowering of T_g on admixture of metals with different atomic radii results in the non-linearity in T_g vs x curves (for small x) for $(\text{Pd}_{1-x}\text{M}_x)_{0.835}\text{Si}_{0.165}$ alloys and in the shift in peak positions of T_g vs x curves of $(\text{Pd}_{1-x}\text{N}_x)_{0.80}\text{P}_{0.20}$ alloys.

Effect of Palladium on the Oxidation Behaviour of Sintered Tungsten-Chromium-Palladium Alloys

T. ITAGAKI and R. YODA, *Nippon Kinzoku Gokkaiishi*, 1974, **38**, (6), 486-492

The effect of Pd on sintering and oxidation behaviour of W-Cr alloys was studied on specimens containing 10-20%Cr, 0.1-2%Pd and 0.1-2%Ni and compared with that of Ni which is an effective activator for sintering of W. Both Pd and Ni accelerated the sintering of W-Cr as well as the sintering of W but Pd was more effective in activating the sintering than Ni.

Crystal Structure of the So-called R.E.₅Pd₂ Compounds

M. L. FORNASINI and A. PALENZONA, *J. Less-common Metals*, 1974, **38**, (1), 77-82

Single-crystal photographic data of the crystal

structure of Dy_5Pd_2 show that this compound is cubic with $a=13.529\text{\AA}$, space group $Fd\bar{3}m$, and the elementary cell containing 68 Dy and 28 Pd atoms. The $\text{R.E.}_5\text{Pd}_2$ compounds, where R.E. = Tb, Ho, Er, Tm, Lu, and Y, are isotypic with Dy_5Pd_2 , and their lattice values are reported.

The Growth and Structure of Epitaxial Rhodium Films

R. F. MILLER and J. KOSHY, *J. Phys. D: Appl. Phys.*, 1974, **7**, (11), 1472-1474

Single-crystal Rh films were epitaxially grown by vacuum evaporation on the cubic, octahedral and dodecahedral planes of rock salt, and also on Ag. The structure of the films was investigated by electron microscopy as a function of substrate temperature and thickness of 28-600°C and 10-600 Å, respectively.

Oxidation of Iridium

R. T. WIMBER and H. G. KRAUS, *Metall. Trans.*, 1974, **5**, (7), 1565-1572

Ir wires heated by self resistance at 1675-2260°C were oxidised in naturally convected O_2 at 0.00132-1.32 atm. The experimental results were correlated by a theoretical rate equation based on control of the oxidation rates by diffusion of Ir(g) , $\text{IrO}_2(\text{g})$ and $\text{IrO}_3(\text{g})$ through the gaseous boundary layer. Standard-state free-energies of $\text{IrO}_2(\text{g})$ and $\text{IrO}_3(\text{g})$ formation were obtained.

Phase Diagram of the Iridium-Zirconium System

V. V. KUPRINA and G. I. KUPYACHAYA, *Vest. Moskov. Univ., Ser. II, Khim.*, 1974, **15**, (3), 371-373

Studies of the Zr-Ir system detected the intermediate phases ZrIr_3 , ZrIr_2 , ZrIr , Zr_2Ir , and Zr_3Ir . ZrIr_3 , ZrIr_2 and Zr_3Ir are formed by peritectic reactions. ZrIr is formed directly and undergoes the polymorphic conversion $\beta \rightarrow \alpha$.

Investigation of the Character of the Interatomic Interaction in Alloys of the Ruthenium-Vanadium System

V. K. YURTAeva, G. P. MURAV'eva, M. V. RAEVSKAYA, I. G. SOKOLOVA and E. M. SOKOLOVSKAYA, *Vest. Moskov. Univ., Ser. II, Khim.*, 1974, (4), 464-466

The probability of stacking fault formation in Ru-V alloys in the V solid solution range was studied and a relation between stacking faults and alloy hardness was detected.

Density of Molten Palladium, Platinum, and Iridium at the Melting Point

P. S. MARTSENYUK and YU. N. IVASHCHENKO, *Ukr. Khim. Zh.*, 1974, **40**, (4), 431-433

Densities of molten Pd, Pt and Ir measured at the melting point were found to be 10.52, 18.81 and 19.39 Mg/m^3 for Pd, Pt and Ir, respectively. The impurity contents of the metals were 0.050%Pd, 0.021%Pt and 0.030%Ir.

CHEMICAL COMPOUNDS

Structure-Activity Relationships for Antitumour Active Platinum(II) Complexes

J. D. HOESCHELE, *Abstr. Papers, 168th Nat. Mtg., Am. Chem. Soc., 1974, (Sept.), INOR 16*

At least three new major classes of antitumour active Pt(II) complexes analogous to *cis*-Pt(NH₃)₂Cl₂ have been identified; [Pt(amine)₂X₂], X₂ = malonates, oxalate; *cis*-(PtA₂Cl₂), A = alicyclic amines; and the "Platinum Blues" - an uncharacterised class of Pt(NH₃)₂-pyrimide complexes.

Chemistry and Antitumour Activity of "Platinum Blue" Complexes

R. G. FISCHER and H. J. PERESIE, *Abstr. Papers, 168th Nat. Mtg., Am. Chem. Soc., 1974, (Sept.), INOR 17*

The reaction of *cis*-diaquodiammine Pt(II) with 2,4-dihydroxypyrimidines and primary amides leads to the formation of highly coloured complexes of Pt which are different in type from the classic "Platinum Blue" complexes. The results of chemical and spectral studies on these complexes are given and are related to possible structures for these complexes.

Potential Anti-cancer Activity of Platinum and Palladium Amine Complexes

S. KIRSCHNER and A. MAURER, *Abstr. Papers, 168th Nat. Mtg., Am. Chem. Soc., 1974, (Sept.), INOR 94*

The preparation of Pd and Pt complexes with morpholine, piperazine and piperidine ligands, which show some biological activity but which do not exhibit anti-tumour activity in their own right, is reported. Complexes containing hydrazine as a ligand were also prepared and characterised before screening for anti-cancer activity.

Evidence for Ordered Layers of K⁺ in KCP (K₂[Pt(CN)₄]Cl_{0.3}·3H₂O)

H. J. DEISEROTH and H. SCHULZ, *Phys. Rev. Lett., 1974, 33, (16), 963-965*

The crystal structure of K₂[Pt(CN)₄]Cl_{0.3}·3H₂O was determined. It crystallises in space group *P4mm*, contrary to earlier assignments. The K⁺ ions occupy ordered positions in layers with a periodicity of *c* = 5.77 Å which are perpendicular to the *c* axis. The same kind of superstructure was found for K₂[Pt(CN)₄]Br_{0.3}·3H₂O.

Observation of Electromagnetic Resonances in Crystals of K₂Pt(CN)₄Br_{0.3}·3H₂O at Microwave Frequencies

R. C. JAKLEVIC and R. B. SAILLANT, *Solid State Commun., 1974, 15, (2), 307-312*

Electromagnetic dielectric resonances in the range 8-11 GHz have been observed in 1 mm sized crystals of K₂Pt(CN)₄Br_{0.3}·3H₂O. This

observation results directly from the existence of large dielectric constants; values for the longitudinal and transverse dielectric constants at 4 K are $\epsilon_{||} \approx 3000$ and $\epsilon_{\perp} \approx 4$.

On Fluoropalladates(II) KPdF₃, RbPdF₃, TIPdF₃ and K₂PdF₄

E. ALTER and R. HOPPE, *Z. Anorg. Allgem. Chem., 1974, 408, (2), 115-120*

RbPdF₃, TIPdF₃ and KPdF₃ were obtained by heating the binary fluorides in a closed system; lattice parameters and the colour of the compound in each case are given.

Composition and Stability of Osmium(IV)-Amino Acids Complexes

O. FAROOQ and N. AHMAD, *J. Electroanal. Chem. Interfac. Electrochem., 1974, 53, (3), 461-464*

The interaction of Os(IV) with some amino acids using sodium chloroosmate in an aqueous medium was studied. pH measurement and potentiometric titrations were used to calculate the successive equilibrium constants, the overall stability constants, and the compositions.

ELECTROCHEMISTRY

Effect of Chemisorbed Carbon Monoxide on Hydrogen Adsorption at Platinum Electrodes

M. W. BREITER, *Extended Abstr., 145th Mtg., Electrochem. Soc., 1974, 74-1, (May), 730-731, abstr. 303*

Studies of the effect of chemisorbed CO on H adsorption on Pt electrodes at room temperature showed that the potential-H coverage plots did not change their shape much on the three electrodes at CO coverages below 0.4. Theoretical predictions require a larger effect than that observed at $\theta_{CO} \leq 0.4$.

Clad Metal Anodes

R. BABOIAN, *Extended Abstr. 145th Mtg., Electrochem. Soc., 1974, 74-1, (May), 601-602, abstr. 256*

Studies of the anodic polarisation behaviour and the stability of the clad metal electrodes (consisting mainly of Pt coatings on Ta, Nb and Ti) using Pt group metals and some of their alloys were conducted in HCl.

Chemisorptive and Catalytic Properties of Platinum-Rhodium Alloys

D. A. J. RAND and R. WOODS, *Extended Abstr., 145th Mtg., Electrochem. Soc. 1974, 74-1, (May), 734-735*

Studies of the electrocatalytic activity of Pt-Rh electrodes during methanol oxidation showed that at 0.58V the activity versus composition curve passes through a maximum at 34%Rh-Pt. The catalytic behaviour is interpreted as a mechanism involving reaction between organic intermediates and hydroxyl radicals adsorbed on the alloy surface.

ELECTRODEPOSITION AND SURFACE COATINGS

Refractory Intermetallic Compound Coatings

P. J. FICALORA, V. SRIKRISHNAN and L. PECORA, *U.S. Rept. AD 774893/2GA*, 1974, 20pp

Crystal structure, electronic configuration and thermodynamics of HfPt₃ and ZrPt₃ were studied. Films of HfPt₃ and ZrPt₃ are suitable for coatings for components subjected to high temperature oxidising atmospheres.

Electron Microscope Investigation of Mixed Stannous Chloride/Palladium Chloride Catalysts for Plating Dielectric Substrates

N. FELDSTEIN, M. SCHLESINGER, N. E. HEDGECOCK and S. L. CHOW, *J. Electrochem. Soc.*, 1974, **121**, (6), 738-744

Electron microscopy and electron diffraction studies of surfaces treated by the catalysing system (SnCl₂/PdCl₂/HCl) in conjunction with various accelerating solutions show that the best plating results are obtained when Pd₃Sn is present on the treated surface prior to the metallisation step.

Kinetics of the Electrodeposition of Palladium

J. A. HARRISON, H. B. S. ALCAZAR and J. THOMPSON, *J. Electroanal. Chem. Interfacial Electrochem.*, 1974, **53**, (1), 145-150

Surface area changes which occur when Pd is deposited on to Pd from chloro-complexes were studied electrochemically. A three-dimensional nucleation and growth model is used to evaluate the kinetics of the process.

HETEROGENEOUS CATALYSIS

Effect of Addition of Iridium on the Activity of Platinum/Alumina Catalysts in the Dehydrogenation of Cyclohexane

N. S. KOZLOV, L. YA. MOSTOVAYA and G. A. ZHIZHENKO, *Neftekhimiya*, 1974, **14**, (4), 591-594

Studies of the effects of Ir additions to Pt/Al₂O₃ on catalyst activity, thermal stability and resistance to S poisoning during cyclohexane dehydrogenation showed that Pt-Ir/Al₂O₃ possesses greater thermal stability and resistance to the action of S compounds than does Pt/Al₂O₃.

Activity of Platinum Catalysts, Prepared on Supports of Type L Dealuminised Zeolites, in the Reactions of Isomerisation and Dehydroisomerisation

L. P. SHIRINSKAYA, V. S. KOMAROV, I. I. URANOVICH, M. F. RUSAK and N. S. KOZLOV, *Neftekhimiya*, 1974, **14**, (4), 568-571

Isomerisation activity of Pt/type L dealuminised zeolites rises with increases in the amount of

dealuminisation and reaches its maximum when SiO₂:Al₂O₃=7.3. Increased dealuminisation of these zeolites leads to a decrease in the dehydrogenation activity of the Pt catalysts.

Conversion of Cyclic Hydrocarbons on Platinum/Alumina Catalyst

R. A. BAKULIN, M. E. LEVINTER and F. G. UNGER, *Neftekhimiya*, 1974, **14**, (5), 707-713

Diene condensation products tend to form on Pt/Al₂O₃ for diene, cyclo-olefin, indene, acenaphthalene, phenanthrene, and anthracene hydrocarbons. Indane, indene, acenaphthalene, phenanthrene, anthracene, and more condensed structures appear to form by C₆- and C₅-dehydrocyclisation of paraffins, alkylaromatic hydrocarbons and diene condensates of intermediate dienes and cyclo-olefins. Coke formation on Pt/Al₂O₃ tends to occur in the order: cyclopentadiene > indene > indane > methylcyclopentane > *bis*-butylbenzene > hexene > decalin > hexane > d-methylnaphthalene > styrene > tetralin.

Effect of Pore Diameter of Aluminium Oxide on the Activity, Stability and Selectivity of Platinum/Alumina Catalysts

V. G. DYRIN, M. E. LEVINTER, A. N. LOGINOVA and L. I. VLASOVA, *Neftekhimiya*, 1974, **14**, (5), 714-719

Fine-pore catalysts have greater activity and stability for aromatisation, hydrocracking and coke formation of petroleum fractions but less selectivity because of increased Pt dispersion and filling of the pores by molecules of the reactants. Fine-pore catalysts have less selectivity than wide-pore catalysts because of secondary aromatisation, transposition of H₂, hydrocracking, and destructive polycondensation with coke formation.

On a New Platinum on Alumina Catalyst. I. Preparation and Composition of the Catalyst

C. HOANG-VAN, P. A. COMPAGNON and S. J. TEICHNER, *Bull. Soc. Chim. Fr.*, 1974, (7-8 pt.1), 1225-1228

Finely divided Pt was deposited on Al₂O₃ without any change in the amorphous state of the support. The amounts of Pt and Cl contained in the samples were determined, as was their specific surface area by the adsorption of N₂.

On the Activity of the Platinum Group Metals in the Demethylation of Toluene with Water Vapour

G. L. RABINOVICH, G. V. DYDYKINA, G. N. MASLYANSKII and M. I. DEMENT'EVA, *Kinet. Kataliz.*, 1974, **15**, (4), 949-953

Pt metals on γ-Al₂O₃ catalyse demethylation of toluene with H₂O vapour. Catalyst activity decreases in the order Rh > Pt > Pd > Ir, Ru, Os, as for demethylation in He. The catalysts are considered to be bifunctional, the metal possessing destructive activity and the support possessing hydrophilic properties.

Determination of the Surface of Dispersed Platinum Catalysts on Electrically Conducting Supports

N. A. URISSEON, L. N. MOKROUSOV, G. V. SHTEINBERG, Z. I. KUDRYAVTSEVA, I. I. ASTAKHOV and V. S. BAGOTSKII, *Kinet. Kataliz*, 1974, **15**, (4), 1009-1014

The specific surface σ in m^2/g for Pt supported on active C, graphite and C black was determined by four independent methods. Supported Pt has 2-4 times the surface of Pt black; σ tends to increase as the Pt concentration decreases.

Adsorption of Hydrogen on Pt/Zeolite Catalysts

T. G. MARTYNYUK, V. I. SHEKHOBALOVA and V. S. BORONIN, *Vest. Moskov. Univ., Ser. II, Khim.*, 1974, (4), 450-454

Studies of the mechanism of H_2 chemisorption on various Pt/zeolite catalysts with respect to Pt content, zeolite type and method of application of Pt to the zeolites showed complexity of adsorption isotherms.

Crystallite Size Effects in the Low-temperature Oxidation of Ammonia over Supported Platinum

J. J. OSTERMAIER, J. R. KATZER and W. H. MANOGUE, *J. Catalysis*, 1974, **33**, (3), 457-473

The effect of crystallite size on the specific catalytic activity of supported Pt catalysts in NH_3 oxidation with O_2 was determined. Rates of NH_3 oxidation were measured in a differential, fixed bed, flow reactor at 393-473 K and catalysts with crystallite size of 20, 27 and 155 Å were used. The initial specific catalytic activity of the 155 Å catalyst was higher than those of the 20 and 27 Å catalysts by factors of 5.7 and 3.7, respectively.

Deactivation of a Platinum Monolithic Carbon Monoxide/Hydrocarbon Oxidation Catalyst

D. LIEDERMAN, S. E. VOLTZ and P. W. SNYDER, *Ind. Engng. Chem., Prod. Res. Dev.*, 1974, **13**, (3), 166-172

The effects of ageing on the CO/hydrocarbon oxidation activity and important physical properties of a Pt monolithic catalyst were determined. Catalyst samples were aged to 25,000 equivalent miles at a maximum temperature of 1450°F with unleaded fuel on an engine dynamometer. The activity for the oxidation of CO, C_2H_6 , and engine exhaust gas hydrocarbons decreased rapidly during the first 1000-5000 miles with very little additional deactivation during further ageing. A large decrease in C_3H_8 oxidation activity continued through the 25,000 miles of ageing. The growth of very large Pt crystallites appeared to be a primary cause of catalyst deactivation. No significant changes in surface area or solid-state phase composition were noted. Small amounts of Pb were detected on aged catalyst samples.

Heats of Adsorption of Hydrogen on Skeleton Platinum, Rhodium and Platinum-Rhodium Catalysts in Hydrochloric Acid Solutions

T. M. GRISHINA, L. I. LOGACHEVA, T. V. SHESTAKOVA and G. D. VOVCHEENKO, *Zh. Fiz. Khim.*, 1974, **48**, (8), 2093-2096

The heats of adsorption of H_2 on skeleton Pt, Rh and Rh-Pt catalysts in 1N HCl solutions were determined and the bonding energies between the adsorbed H_2 and the surfaces were calculated.

Effect of Temperature on the Adsorption of Hydrogen by Skeleton Platinum-Rhodium Catalysts in Hydrochloric Acid Solutions

T. M. GRISHINA, L. I. LOGACHEVA, T. V. SHESTAKOVA and G. D. VOVCHEENKO, *Zh. Fiz. Khim.*, 1974, **48**, (9), 2330-2332

Galvanostatic and potentiodynamic studies of H_2 adsorption on Pt, Rh and Rh-Pt skeleton catalysts in 1N HCl at 10-70°C showed that the adsorption capacity for H_2 on heating is significantly diminished on Rh and Rh-rich alloys.

Effect of the Composition and Conditions of Heat Treatment of Palladium-Rhodium Alloys on Their Catalytic Activity in the Dehydrogenation of Cyclohexane

E. V. KHRAPOVA, V. M. GRYAZNOV, R. O. MZEE, N. R. ROSHAN and B. DZHUNTINI, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1974, (10), 2182-2188

Catalytic activity for cyclohexane dehydrogenation of 7-20%Rh-Pd alloys decreases as H_2 is removed from them and is completely reduced after treatment by H_2 . The activity increases with the temperature for treatment in air from 350 to 750°C. Activity increased after tests at 450-470°C in a stream of Ar, presumably due to the removal of firmly adsorbed H_2 .

The Catalytic Chemistry of Nitric Oxide. II. Reduction of Nitric Oxide over Noble Metal Catalysts

T. P. KOBYLINSKI and B. W. TAYLOR, *J. Catalysis*, 1974, **33**, (3), 376-384

The reduction studies of NO with H_2 , CO, and equimolar mixture of H_2/CO over supported Pt, Pd, Rh, and Ru catalysts showed that when H_2 was used the activity of the catalyst was $\text{Pd} > \text{Pt} > \text{Rh} > \text{Ru}$. When CO or CO/H_2 mixtures were used, this activity sequence was reversed. The results show that CO inhibits NO reduction strongly over Pt and Pd, the presence of CO over Ru catalyst accelerates the reaction and the reduction of NO in the presence of Pt and Pd gives NH_3 as major product.

Hydrogenation of Allyl Alcohol on Rhodium

A. M. SOKOL'SKAYA, K. KH. NURGOZHAEV and T. OMARKULOV, *Zh. Fiz. Khim.*, 1974, **48**, (7), 1740-1742

The rate of hydrogenation of allyl alcohol on Rh

black is high because of weakly adsorbed H₂ on the Rh surface. Greatest yield (93%) of propanol occurred at 20°C, 20 atm H₂; greatest yield of propanol occurred at 20°C and 80°C, 60 atm.

Hydrogenation of Aliphatic Ketones under Pressure of Hydrogen

A. M. SOKOL'SKAYA, A. I. LYASHENKO and A. K. ZHARMALAMBETOVA, *Zh. Fiz. Khim.*, 1974, **48**, (8), 2116-2118

1 wt.% Ru/ γ -Al₂O₃ in H₂O at 20-100 atm H₂ supports a high rate of conversion of acetone and methyl ethyl ketone to saturated secondary alcohols. To increase the rate of ketone hydrogenation the H₂ is stabilised by Ru using an alkaline solvent. Hydrogenation takes place by the formation of free radicals not exposed to condensation.

Hydrogenation of Epoxycyclododecadiene over Group VIII Metals

F. A. CHERNYSHKOVA, D. V. MUSHENKO, E. G. LEBEDEVA and V. V. SEMENOVA, *Neftekhimiya*, 1974, **14**, (5), 677-681

Hydrogenation of epoxycyclododecadiene (*trans*-epoxy-*cis*,*trans*-cyclododecadiene) on Group VIII metals takes place at the double bonds in two stages; first to the *cis* and *trans* forms of epoxycyclododecene, which is then reduced to epoxycyclododecane. Yield of the latter is 87-96% on Pd, Ru, Rh, or Pt. Oxirane rings are not reduced on these catalysts. Hydrogenation of the *cis* and *trans* double bonds of epoxycyclododecadiene and epoxycyclododecene on Pd and Rh proceeds at similar rates.

Catalytic Transfer Hydrogenation

G. BRIEGER and T. J. NESTRICK, *Chem. Rev.*, 1974, **74**, (5), 567-580

Studies of the catalytic transfer hydrogenation with an organic molecule as H donor, using Pd but occasionally also Raney Ni showed that this reaction permits the reduction of olefins, nitriles and nitro compounds, as well as hydrogenolysis of benzylic and allylic functional groups and the replacement of aromatic halogen. The reaction is more selective than regular hydrogenation and in special cases, such as the reduction of polyunsaturated steroids, has proved superior.

HOMOGENEOUS CATALYSIS

Investigation of the Catalytic Action of Pt-Sn(II) Complexes in Hydrogenations of Acetylene Hydrocarbons

N. V. BORUNOVA, L. KH. FREIDLIN, YA. G. MUKHTAROV and N. I. MALOFEEV, *Neftekhimiya*, 1974, **14**, (4), 572-575

Pt-Sn complexes catalyse a higher rate of hydrogenation for mono-substituted C \equiv C bonds than for disubstituted, irrespective of the length of the substituted alkyl chain. The amount of hydrogenation of pentyne-1 and phenylacetylene

is closely connected with catalyst concentration and with the pressure of H₂. Monoalkylacetylenes and phenylacetylene are hydrogenated in stages, and diphenylacetylene adds two moles of H₂ via the intermediate stage of diphenylethylene.

Tetrakis(triphenylphosphine)palladium(0) — Homogeneous Catalyst for the Hydrogenation of Acetylene and Ethylene

G. K. SHESTAKOV, A. M. VASIL'EV, L. M. TISHCHENKO, O. N. TEMKIN and R. M. FLID, *Kinet. Kataliz*, 1974, **15**, (4), 1070-1072

Tetrakis(triphenylphosphine)palladium(0) in *o*-xylene effectively catalyses hydrogenation of C₂H₂ and C₂H₄ at 100°C, 1 atm. Butene in the product is formed by hydrodimerisation of C₂H₂ and C₂H₄. The reducing agent may be toluene sulphate and formamide.

Polymerisation of Some Cycloolefins with Palladium- π -complexes

F. HOJABRI, *Abstr. Papers, 168th Nat. Mtg., Am. Chem. Soc.*, 1974, (Supt.), INDE 44

Studies of the Pd π -allylic complexes prepared by the reaction of PdCl₂ with pinenes at high temperature showed them to be very active catalysts for the polymerisation of bicyclohepta-(2,5)-diene at 130-200°C. The polymerisation pattern revealed that only one double bond of the diene was opened by this reaction.

Catalysis by Supported Transition Metal Complexes. II. Hydrogenation of Allyl Alcohol on a Palladium Resin

R. L. LAZCANO, M. P. PEDROSA, J. SABADIE and J.-E. GERMAIN, *Bull. Soc. Chim. Fr.*, 1974, (5-6 pt. II), 1129-1132

The liquid phase hydrogenation of allyl alcohol in the presence of a catalyst obtained by ion exchange with a basic resin having a PdCl₂²⁻ anion gives a mixture of propanol and the corresponding aldehyde. The activity and selectivity of the catalyst was studied as a function of solvent, temperature (25-28°C), H₂ pressure (1-100 bar), and was compared with those of the usual Pd catalysts. Differences in results indicate the presence on the resin of active centres, with markedly different properties to highly dispersed Pd.

The Selectivity of Palladium(II) in Substitution Reactions of Their Chloro-complexes with Diamines

R. ERNST and R. ROULET, *Chimia*, 1974, **28**, (7), 347-349

The rate constants of the substitution reactions of Cl⁻ and H₂O by various diamines in Pd(II) chloro-complexes were determined spectrophotometrically. The substitution mechanism is associative, and comparison with the corresponding Pt(II) complexes shows the selectivity of Pd(II) to be smaller than that of Pt(II).

Rhodium Carbonyl Chloride Anion, $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$: a True Catalyst in the Reduction of NO by CO

C. D. MEYER, J. REED and R. EISENBERG, *Abstr. Papers, 168th Nat. Mtg., Am. Chem. Soc., 1974*, (Sept.), INOR 116

Studies of the $\text{RhCl}_3/\text{EtOH}$ catalyst during reduction of NO by CO showed that addition of HCl to the catalyst system shortens an induction period, during which $\text{Rh}(\text{CO})_2\text{Cl}_2^-$ is formed, and acid accelerates the reaction between NO and CO. The interaction of $\text{Rh}(\text{CO})_2\text{Cl}_2^-$ with NO has been examined and i.r. spectroscopy reveals the presence of several nitrosyl species.

Preparation of Hydridometalloboranes and Their Use as Homogeneous Catalysts

T. E. PAXSON and M. F. HAWTHORNE, *J. Am. Chem. Soc.*, 1974, **96**, (14), 4674-4676

Methanol solution of the tris(triphenylphosphine)rhodium(I) cation was reacted at 60°C with a methanolic solution of either $(\text{CH}_3)_3\text{NH}^+[7,8-\text{C}_2\text{B}_9\text{H}_{12}]^-$ or $(\text{CH}_3)_3\text{NH}^+[7,9-\text{C}_2\text{B}_9\text{H}_{12}]^-$ and high yields of 3,3- $[(\text{C}_6\text{H}_5)_3\text{P}]_2-3-\text{H}-3,1,2-\text{RhC}_2\text{B}_9\text{H}_{11}$ and 2,2- $[(\text{C}_6\text{H}_5)_3\text{P}]_2-2-\text{H}-2,1,7-\text{RhC}_2\text{B}_9\text{H}_{11}$, respectively, were obtained. These compounds catalyse the deuterium exchange of terminal {BH} groups in boranes, carboranes and metalloboranes, and the hydrosilation of ketones.

Transition Metal Catalysed Exchange of Deuterium Gas with Terminal Boron-Hydrogen Bonds in Carboranes, Metalloboranes, and Other Boron Compounds

E. L. HOEL and M. F. HAWTHORNE, *Ibid.*, 4676-4677

In the presence of catalytic amounts of $(\text{PPh}_3)_3$, RuHCl which is an effective catalyst for the specific ortho deuteration of triphenylphosphine, carboranylphosphine was found to exchange H atoms for deuterium gas at B atoms but not at Ca atoms. The nucleophilic character of transition metal complexes in ortho metallation and other oxidative additions was discussed.

Homogeneous Catalysis of Hydrogen Isotope Exchange between D_2 and Ethanol by Chlorotris(triphenylphosphine)rhodium(I). I. In Benzene-Ethanol

G. STRATHDEE and R. GIVEN, *Can. J. Chem.*, 1974, **52**, (12), 2216-2225

The kinetics and mechanism of $\text{D}_2-\text{C}_2\text{H}_5\text{OH}$ exchange catalysed by $\text{RhCl}(\text{Ph}_3\text{P})_3$ was studied in 50 vol.-% $\text{C}_6\text{H}_6-\text{C}_2\text{H}_5\text{OH}$. The exchange rate was low and was limited by the D_2 transfer rate from diduteriodichlorotris(triphenylphosphine)rhodium(III) to the solvent, and not by the rate of activation of D_2 . The activation energy for the overall process = 35 kJ/mol. New data is given for the catalysis of H_2-D_2 exchange in C_6H_6 by $\text{RhCl}(\text{Ph}_3\text{P})_3$. Analysis of the apparent HD: D_2 isotope effect observed during $\text{D}_2-\text{C}_2\text{H}_5\text{OH}$

exchange suggests that this effect originates from the relative stabilities of the D_2 , HD and H_2 adducts with $\text{RhCl}(\text{Ph}_3\text{P})_3$, or by control of the HD and H_2 product distribution by the H_2-D_2 equilibrium reaction.

Homogeneous Catalysis of Hydrogen Isotope Exchange between D_2 and Ethanol by Chlorotris(triphenylphosphine)rhodium(I), II. In Chloroform-Ethanol

Ibid., 2226-2235

The kinetics and mechanism of D_2 exchange catalysed by $\text{RhCl}(\text{Ph}_3\text{P})_3$ was studied in $\text{CHCl}_3-\text{C}_2\text{H}_5\text{OH}$ solutions. The D_2 exchange reaction rate is strongly dependent on solvent composition and decreased 30 times between 6-96 mol.-% $\text{C}_2\text{H}_5\text{OH}$. The activation energy for D_2 exchange = 101 ± 9 kJ/mol at 58 mol.-% $\text{C}_2\text{H}_5\text{OH}$, and 86 ± 8 kJ/mol at 6 mol.-% $\text{C}_2\text{H}_5\text{OH}$. Results thus indicate solvent-catalyst bonding interactions to be important in this respect.

Homogeneous Catalysis of Olefin Isomerisation. Part IV. The Isomerisation of Pent-1-ene Catalysed by Solutions of $\text{IrH}(\text{CO})(\text{PPh}_3)_3$, $\text{IrHCl}_2(\text{PEt}_2\text{Ph})_3$, $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$, $\text{IrCl}(\text{O}_2)(\text{CO})(\text{PPh}_3)_2$, and of $\text{PtH}(\text{SnCl}_3)(\text{PPh}_3)_2$

D. BINGHAM, D. E. WEBSTER and P. B. WELLS, *J. Chem. Soc., Dalton Trans.*, 1974, (14), 1514-1518

The isomerisation of pent-1-ene to pent-2-ene at 80°C is catalysed by solutions of (1) $\text{IrH}(\text{CO})(\text{PPh}_3)_3$, (2) $\text{IrHCl}_2(\text{PEt}_2\text{Ph})_3$, (3) $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ or $\text{IrCl}(\text{O}_2)(\text{CO})(\text{PPh}_3)_2$ each in the presence of O source, and (4) $\text{PtH}(\text{SnCl}_3)(\text{PPh}_3)_2$ in benzene. System (1), (2) and (4) catalyse the preferential formation of *cis*-pent-2-ene where as (3) provides preferential formation of *trans*-pent-2-ene.

Part V. Pent-1-ene Isomerisation Catalysed by Solutions of $\text{RuHCl}(\text{PPh}_3)_3$ and of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$; Variation of the Isomeric Composition of Pent-2-ene and Its Attribution to Steric Factors

Ibid., 1519-1521

Isomerisation of pent-1-ene to pent-2-ene at 35-80°C is catalysed by solutions of $\text{RuHCl}(\text{PPh}_3)_3$ and $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ in benzene. Preferential formation of *cis*-olefin occurs at higher catalyst concentrations but a change to preferential *trans*-olefin formation is observed as catalyst concentration is reduced.

Part VI. Pent-1-ene Isomerisation Catalysed by Solutions of Dodecacarbonyltri-iron(0) and of Bis(benzonitrile)dichloropalladium (II) in Benzene

D. BINGHAM, B. HUDSON, D. E. WEBSTER and P. B. WELLS, *Ibid.*, 1521-1524

Isomerisation of pent-1-ene to *cis*- and *trans*-pent-2-ene is catalysed at 50°C and above by solutions in benzene of $\text{Fe}_3(\text{CO})_{12}$ and of PdCl_2

(C₆H₅CN)₂. In both cases, preferential formation of *trans*-pent-2-ene occurs. The reaction mechanisms involve π -allylic intermediates; for the Pd-catalysed reaction bis- π -allyl complexes may also participate.

Homogeneous Hydrogenation of Buta-1,3-diene and Ethylene Catalysed by Carbonylhydridotris(triphenylphosphine)iridium(I) and by Carbonyltrihydridobis(triphenylphosphine)iridium(III)

M. G. BURNETT, R. J. MORRISON and C. J. STRUGNELL, *J. Chem. Soc., Dalton Trans.*, 1974, (16), 1663-1671
Spectrophotometric and kinetic studies of the individual steps in the catalytic cycle of buta-1,3-diene hydrogenated to a mixture of butenes and butane by IrH(CO)(PPh₃)₃ and IrH₃(CO)(PPh₃)₂ at 50°C in dimethylformamide, were quantitatively interpreted in terms of a mechanism based on the reductive elimination of butenes by Ir(σ -C₄H₇)H₂(CO)(PPh₃)₂. The intermediate Ir(π -C₄H₇)(CO)(PPh₃)₂ was also isolated and characterised.

Complex Metal-Polymer Catalysts for Benzene Hydrogenation

E. N. RASADKINA, T. V. KUZNETSOVA, A. T. TELESHEV, I. D. ROZHDESTVENSKAYA and I. V. KALECHITS, *Kinet. Kataliz.*, 1974, 15, (4), 969-973
Studies of Rh, Ir and Pd catalysts complexed with nylon showed how conditions of their preparation affect their properties in C₆H₆ hydrogenation. Cyclohexene is formed as well as cyclohexane. The order of activity of these complexes is Ir > Pt > Rh > Pd.

NEW PATENTS

METALS AND ALLOYS

Palladium Alloy for Hydrogen Membranes

URALSKY ORDENA TRUDORAGA KRASNOGO ZNAMEI POLITEKHNICHESKY INSTITUT
British Patent 1,365,271

Alloys for H diffusion contain 1-26% Ag, 1-26% Au, 0.1-0.9% Ru, 0.1-2% Al and 0.1-2.5% Pt, remainder Pd. In one example an alloy contains 75% Pd, 20% Ag, 2.5% Au, 0.5% Ru, 1% Al and 1% Pt.

CHEMICAL COMPOUNDS

Synthesis of Silyl Metal Complexes

DOW CORNING CORP. *British Patent* 1,363,158
Silyl Pt and Pd complexes are formed by reacting disilanes or hydrosilanes with Pt or Pd phosphine complexes. Thus Si₂Cl₆ with Pd(PPh₂Me)₂Cl₂ gives Pd(PPh₂Me)₂(SiCl₃)Cl.

CHEMICAL TECHNOLOGY

Morphology of Dimensionally Stable Anodes

K. J. O'LEARY and T. J. NAVIN, *Extended Abstr.*, 145th Mtg., *Electrochem. Soc.*, 1974, 74-1, (May), 603-608, abstr. 257

X-ray studies of 2:1 molar ratio solutions of Ti and Ru painted on a clean Ti substrate and fired at 100-700°C showed that below 300°C they are amorphous and above 700°C they are fully crystalline with extremely small crystals of 100-500Å. Electrical conductivity of fully crystalline solid solutions falls between the insulator TiO₂ and metallic conductor RuO₂.

ELECTRICAL AND ELECTRONIC ENGINEERING

Reliability Studies of the PtSi-Ta-Au Metalisation System for Microwave Power Transistors

H. M. DAY, A. CHRISTOU, W. WEISENBERGER and J. K. HIRVONEN, *Extended Abstr.*, 145th Mtg., *Electrochem. Soc.*, 1974, 74-1, (May), 188-189, abstr. 75

X-ray and electron diffractometry studies of the Si-Ta-Pt-Au and Si-Pt layers showed formation of TaAu, Ta₂Si and Ta₂Pt compounds at >450°C, while PtSi formed at the Si-Pt interface at 200°C in 20 min. The ion backscattering data indicate that no further reaction takes place at the Si-Pt interface when annealed in vacuum at 700°C. Auger electron data on the Si-Ta-Pt-Au system are also obtained and discussed.

ELECTRODEPOSITION AND SURFACE COATINGS

Ruthenium Dioxide Electrode Coating

ELECTRONOR CORP. *British Patent* 1,370,529
Finely-divided RuO₂ having a particulate size of 0.1 μ or less dispersed in an organic polymer, resistant to degradation in an electrolytic process exhibits a low oxygen overvoltage for a surprisingly long period of time. Also a combination of finely-divided RuO₂ and organic polymer on an electrically-conductive substrate provides an efficient electrode for many electrochemical reactions.

HETEROGENEOUS CATALYSIS

Aromatic Hydrogenation

TEXACO DEVELOPMENT CORP.
British Patent 1,363,179
The hydrogenation of aromatic hydrocarbons in