

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Order-Disorder Transformation in CuPt

E. TORFS, L. STALS, J. VAN LANDUYT, P. DELAVIGNETTE and S. AMELINCKX, *Phys. Status Solidi A - Appl. Res.*, 1974, 22, (1), 45-51

The order-disorder transformation in CuPt was studied by means of electrical resistance measurements, transmission electron microscopy and electron diffraction. In heated disordered CuPt, short range order is developing at 20-190°C by the formation of microdomains which grow into long range order domains after further heating.

Ferromagnetic Properties at High Fields and High Pressures of Nickel-Platinum Alloys near the Critical Concentration for Ferromagnetism

H. L. ALBERTS, J. BEILLE, D. BLOCH and E. P. WOHLFARTH, *Phys. Rev. B*, 1974, 9, (5), 2233-2243

Magnetic properties of ferromagnetic Ni-Pt alloys containing 42.9, 45.2, 47.6 and 50.2 at. % Ni were measured at 4-60 K in magnetic fields up to 60 kOe and pressures up to 7 kbar. The effective interaction U was 0.44 eV while the ratio of U to the bare interaction was 0.65.

Non-equilibrium Phases in Al-rich Al-Pt Alloys

A. M. TONEJC, A. TONEJC and A. BONEFAČIĆ, *J. Mater. Sci.*, 1974, 9, (4), 523-526

X-ray diffraction studies of Pt in Al when the solid solubility of Pt in Al was extended from 0 to 2 at. % by the "two-piston" quenching technique showed an intermediate metastable phase during decomposition. The stability of the Al-Pt solid solution during annealing is also discussed.

Metallurgical Aspects of Binary Alloy Films Grown from the Melt

A. OLIVEI, *Z. Metallkunde*, 1974, 65, (7), 482-488

The properties of solidification structures were studied on 0.16% Si-Pt and the thermodynamics of the steady state solidification in thin and thick binary films were observed. The problem of microsegregation in cellular and dendritic solidification was also studied.

Diffusion of Hydrogen in β -Palladium Hydride at High Pressures

M. KUBALLA and B. BARANOWSKI, *Ber. Bunsenges. Phys. Chem.*, 1974, 78, (4), 335-338

A relaxation method was applied for the deter-

mination of the intrinsic diffusion coefficient of H_2 in β -phase Pd hydride up to 23 kbar of equilibrium H_2 pressure. The activation energies and frequency factors for diffusion obtained from the temperature dependence of the diffusion coefficients at constant pressure exhibit maximum values of 300-400 bar, indicating the occurrence of a diffusive motion no longer definable by a single-jump mechanism between adjacent octahedral interstitials in the Pd lattice.

Experimental Study of the Critical-point Behaviour of the Hydrogen in Palladium System: I. Lattice Gas Aspects. II. Specific Heat

Y. DE RIBAUPIERRE and F. D. MANCHESTER, *J. Phys. C, Solid State Phys.*, 1974, 7, (12), 2126-2139, 2140-2146

For the H_2 in Pd (PdH) system, the critical point was located at $T_c = 566 \pm 1$ K, $p_c = 0.29 \pm 0.01$ atomic H/Pd ratio, $P_c = 19.89 \pm 0.05$ atm (H_2 pressure surrounding Pd). Critical point exponents δ , γ and Δ were determined for the critical isotherm, the isothermal compressibility of the H_2 lattice gas and the relaxation time of the elastic after-effect, respectively. Studies of the specific heat of the PdH system through the critical point region using a temperature wave method showed at constant H_2 concentration a simple discontinuity at the critical point, corresponding to the critical point exponent, α , equal to zero. Results showed that mean-field theory describes the critical point behaviour of PdH.

Superconductivity in PdH, PdD and PdAgD Systems

F. HERTEL, *Z. Physik*, 1974, 268, (2), III-III5

The mechanisms of superconductivity in PdH(D) and PdAgH(D) systems are discussed. The possible participation of the optical phonon modes in the electron-phonon coupling is examined as is their importance for the observed opposite isotope effect in these systems.

High Superconducting Transition Temperatures in the Palladium-Noble Metal-Hydrogen System

B. STRITZKER, *Z. Physik*, 1974, 268, (2), 261-264

High superconducting transition temperatures, T_c , of 16.6, 15.6 and 13.6 K were observed in Pd-Cu, Pd-Ag and Pd-Au alloys, charged with large amounts of H by means of ion implantation at $T_{liq. He}$. A peculiar phase-transition indicates that weak phonon modes might be responsible for

the high T_c values. The difference between the maximum T_c values may be explained as a type of isotope effect $T_c \propto M^{-1/2}$.

Alloys with High Temperature Coefficient of Linear Expansion Mn-Pd Based System

M. P. RAVDEL' and O. I. EVDOKIMOVA, *Metalloved. Term. Obrab. Metal.*, 1974, (5), 36-38

Studies of the temperature coefficient of linear expansion in γ -phase of Mn-Pd and Mn-Pd-Ni alloys showed that in Mn-Pd alloys the coefficient depended on Pd content. The range of concentration for the stable alloy with high temperature coefficient of linear expansion ($36-39 \cdot 10^{-6}/^\circ\text{C}$) was found to be 72-75% Mn, 15% Pd and Ni.

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

T. ITAGAKI and R. YODA, *J. Japan Inst. Metals*, 1974, 92, (6), 486-492

The effect of Pd on the sintering and oxidation behaviour of W-Cr alloys was studied 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 but Pd was more effective.

On the Constitution of the Palladium-Germanium Alloys

K. KHALAFF and K. SCHUBERT, *Z. Metallkunde*, 1974, 65, (5), 379-382

X-ray, microscopic and thermal studies of the Pd-Ge system showed two previously unknown phases, $\text{Pd}_{25}\text{Ge}_9$ and Pd_5Ge_2

X-ray Study of an Amorphous $\text{Pd}_{80}\text{Si}_{20}$ Alloy

P. MRAFKO and P. DUHAJ, *Phys. Status Solidi A - Appl. Res.*, 1974, 22, (1), 151-155

X-ray diffraction studies of the structure of an amorphous $\text{Pd}_{80}\text{Si}_{20}$ alloy obtained by rapid quenching from the liquid state and an analysis of the radial distribution function showed that the first nearest neighbours were located at 2.83, 4.6, 5.5, and 7.7 Å. The number of the first nearest neighbours was 11.7.

A Mass Spectrometric Study of the Sublimation of Rhodium and the Dissociation Energy of the Molecule $\text{Rh}_2(\text{g})$

V. PIACENTE, G. BALDUCCI and G. BARDI, *J. Less-common Metals*, 1974, 37, (1), 123-127

Vapour pressure and derived values of ΔH_{2988}^0 were measured during sublimation of Rh at 1850-2120 K using the Knudsen effusion-mass spectrometric technique. The resulting average $\Delta H_{2988}^0 = 133.9 \pm 0.4$ kcal/g-at. At the higher temperatures the molecule $\text{Rh}_2(\text{g})$ was identified and a value $D_{00}^0(\text{Rh}_2) = 64.7$ kcal/mole for its dissociation energy was determined.

The Growth and Characterisation of High-purity Rhodium Single Crystals

J. J. RUBIN and D. L. MALM, *J. Vacuum Sci. Technol.*, 1974, 11, (1), 389

Studies of magnetic impurity scattering at low temperature were made on high-purity Rh crystals and Rh-Fe alloys grown by electron beam float zoning. Residual gas atmosphere during crystal growth was analysed and the decay of gaseous impurities was observed.

The Activity of Iridium in Iridium-Platinum Alloys by a Transpiration Method

E. S. RAMAKRISHNAN and M. S. CHANDRASEKHARAIHAH, *J. Less-common Metals*, 1974, 37, (2), 269-280

Ir activity in 3-60 wt.% Ir-Pt alloys was determined by a transpiration method at 1468-1518 K using O_2 at 1 atm as the reactive carrier gas. The partial pressures of the volatile IrO_3 in equilibrium with various alloys were determined at each temperature.

CHEMICAL COMPOUNDS

The Preparation and Growth of Pure Crystals of $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}\cdot 3\text{H}_2\text{O}$ and $\text{K}_2\text{Pt}(\text{CN})_4\text{Cl}_{0.3}\cdot 3\text{H}_2\text{O}$

R. B. SAILLANT, R. C. JAKLEVIC and C. D. BEDFORD, *Mater. Res. Bull.*, 1974, 9, (3), 289-294

The preparation of pure single crystals of $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}\cdot 3\text{H}_2\text{O}$ and $\text{K}_2\text{Pt}(\text{CN})_4\text{Cl}_{0.3}\cdot 3\text{H}_2\text{O}$ were studied. Crystals with reproducible d.c. conductivity and dielectric constants were obtained only when the mixed valence Pt salt contained one halide. The best quality crystals were grown by slow evaporation of solutions which were 1 M in urea and 0.1 M in the appropriate K halide.

On the *cis*-Effect in Complex Compounds of Divalent Platinum

N. N. ZHELIGOVSKAYA, S. V. LOGINOV, L. V. POPOV and V. I. SPITSYN, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1974, (6), 1411-1413

Studies of the acidic properties of *cis*-acidoaquo complexes of Pt(II) showed that nitro groups intensify the acidity of *cis*-position H_2O molecules compared to that of similar halo complexes. The stability of *cis*-nitrochloro-, dichloro-, dibromo-, and diiodoethylenediamine complexes of Pt(II) in aqueous solutions was studied. Hydrolysis of PtEnNO_2Cl occurred in fewer stages than hydrolysis of PtEnCl_2 .

Isomerisation of *cis*-Dichlorodiammine-platinum(II) in Aqueous Solution

YU. G. BREUSOVA-BAIDALA, N. N. ZHELIGOVSKAYA and V. I. SPITSYN, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1974, (6), 1239-1242

Studies of ultraviolet spectra of aqueous solutions of *cis*- and *trans*-dichlorodiammineplatinum(II)

showed that UV spectroscopy might be used to identify these isomers. UV and infra-red spectroscopy showed that *cis*→*trans* isomerisation occurs spontaneously in aqueous solutions.

Study of the Kinetics of Isomerisation of *cis*-Dichlorodiammine platinum in Aqueous Solution

Ibid., 1242-1243

The rate of isomerisation of *cis*-dichlorodiammine-platinum(II) in aqueous solution is first order. The rate constant is $(1.06 \pm 0.08) \times 10^{-8}$.

Platinum Bronzes. IV. Preparation, Crystal Chemistry, and Physical Properties

D. CAHEN, J. A. IBERS and J. B. WAGNER, *Inorg. Chem.*, 1974, 13, (6), 1377-1388

The Na and Cd bronzes $\text{Na}_x\text{Pt}_3\text{O}_4$ and $\text{Cd}_x\text{Pt}_3\text{O}_4$ as well as the bronze-like CaPt_2O_4 were prepared in powder form at 1 atm and the existence of Pt_3O_4 was also discussed. Syntheses for $\text{Cd}_x\text{Pt}_3\text{O}_6$ and a poorly defined new simple oxide of Pt with stoichiometry Pt_5O_6 are given.

The Preparation and Characterisation of $\text{CdIr}(\text{OH})_6$ and $\text{ZnIr}(\text{OH})_6$

R. F. SARKOZY and B. L. CHAMBERLAND, *J. Solid State Chem.*, 1974, 10, (2), 145-150

$\text{CdIr}(\text{OH})_6$ and $\text{ZnIr}(\text{OH})_6$ were isolated in the process of synthesising new ternary oxides of the Pt group metals by means of thermal decomposition of hydroxide intermediates. Both compounds crystallise with an ordered ReO_3 -type structure. $\text{CdIr}(\text{OH})_6$ is tetragonal with $a=7.86 \text{ \AA}$ and $c=7.91 \text{ \AA}$ and $\text{ZnIr}(\text{OH})_6$ is cubic with $a=7.64 \text{ \AA}$.

ELECTROCHEMISTRY

Adsorption of Hydrogen by Platinum, Osmium and Their Alloys at Various Temperatures in Hydrochloric Acid Solution

I. N. GOLYANITSKAYA, A. A. SUTYAGINA and G. D. VOVCHEKHO, *Zh. Fiz. Khim.*, 1974, 48, (4), 935-937
Studies of H_2 adsorption on Pt, Os, and 24 and 64 wt.% Os-Pt at 10-70°C showed the sizes of the differential isothermic heats of adsorption and of the bonding energy $g_{\text{Me-H}}$ to the surface. Electrolyte composition has the most effect on these values for Pt and for Pt-rich Os-Pt catalysts.

ELECTRODEPOSITION AND SURFACE COATINGS

The Role of Accelerators prior to Electroless Plating of ABS Plastic

A. RANTELL and A. HOLTZMAN, *Trans. Inst. Metal. Finish.*, 1974, 52, (2), 31-38

Studies in the activation of ABS plastic prior to electroless deposition achieved by treatment with mixed SnCl_2 - PdCl_2 catalysts showed that the

catalytic activity of the ABS surface directly related to the number of catalytic Pd nuclei created. This number depends on the amount of SnCl_2 - PdCl_2 catalyst absorbed, the degree of acceleration and the type of accelerator employed.

HETEROGENEOUS CATALYSIS

Molecular Oxygen Induced Crystallite Size Effect in Reduction of Nitric Oxide with Ammonia over Supported Platinum

R. J. PASATERI, J. R. KATZER and W. H. MANOGUE, *Am. Inst. Chem. Engng. J.*, 1974, 20, (2), 219-227
The effect of changing Pt crystallite size from 2.7 to 15.5 nm on the specific catalytic activity in NO reduction by NH_3 , with and without added O_2 , was studied over $\text{Pt}/\text{Al}_2\text{O}_3$ catalysts at 423-473 K. In the NO- NH_3 system both specific catalytic activity and selectivity to N_2 are independent of crystallite size. In the NO- O_2 - NH_3 system the specific catalytic activity of the 15.5 nm crystallites is 6 times that of the 2.7 nm crystallites. The NO reduction rate shows dependence on NO to the first power, and on NH_3 to the power $\frac{1}{2}$.

Effect of the Addition of Tungsten Oxide on the Activity and Stability of Platinum/Alumina Catalysts in the Aromatisation of Hydrocarbons

V. N. SELEZNEV, YU. V. FOMICHEV and M. E. LEVINTER, *Neftekhimiya*, 1974, 14, (2), 210-204

Addition of WO_3 to $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst increases its activity. Greatest activity occurs when the W content is 0.2 wt.%.

Effect of the Addition of Tin on the Activity and Stability of Platinum/Alumina Catalysts in the Processes of Aromatisation and Reforming

Ibid., 205-208

Sn additions to $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst increase the aromatisation activity, particularly for catalysts with lower Pt contents (0.35 wt.%). Little coke is formed on $\text{Pt}/\text{Al}_2\text{O}_3$ with 0.2 wt.% Sn and so the catalyst is more stable during heptane aromatisation and petroleum reforming than unmodified catalyst.

On the Effect of the Chemical Properties of the Surface of Aluminium Oxide on the Hydrogenating Activity of Platinum/Alumina Catalysts

B. B. ZHARKOV, G. N. MASLYANSKII, T. V. ANTIPINA, V. A. RESHETOV, A. Z. RUBINOV and T. M. KLIMENKO, *Kinet. Kataliz.*, 1974, 15, (3), 732-737

The surface acidity of Al_2O_3 samples calcined at 300-1100°C and the hydrogenation activity of Pt catalysts prepared on this support are inversely related. Chemisorption capacity and hydrogenation activity of these catalysts pass through a minimum corresponding to a calcining tempera-

ture of the Al_2O_3 of 500–700°C. This temperature is that of maximum surface acidity of Al_2O_3 .

Effect of the Acidity of $\gamma\text{-Al}_2\text{O}_3$ on the Properties of Platinum/Alumina Catalysts in the Aromatisation of Methylcyclohexane and *n*-Heptane

V. G. VLASOV, *Neftekhimiya*, 1974, **14**, (2), 209–214

The specific surface and the dispersion of Pt both increase as the acidity of the Al_2O_3 support is raised. The increased yield of aromatic hydrocarbons from paraffins is due not only to the effect of the acidity on the acceleration of the limiting stage of the aromatisation process but to the higher dispersion of Pt in more acid catalysts.

Catalytic Properties of Platinum on Charcoal Carriers of Different Pore Structure

B. PARLITZ and K.-H. SCHNABEL, *Z. Anorg. Allgem. Chem.*, 1974, **405**, (3), 299–306

5% Pt/C catalysts were studied to establish the influence of carrier pore structure and Pt dispersivity on their catalytic properties; test reactions were the dehydrogenation of cyclohexane, and the dehydrocyclisation of three isometric octanes. A biporous carrier characteristic results in optimal activity for cyclohexane dehydrogenation. For octane dehydrocyclisation, pore structure has a strong influence. Microporosity strongly reduces the selectivity of the catalyst system.

Investigations on the Synthesis of the Compound $\text{PtO}_2\cdot 4\text{CaO}$ and Its Catalytic Properties in the Process of Ammonia Oxidation

A. KOLACZKOWSKI, J. KUBICKI and M. SZUSTAKOWSKI, *Chem. Stosowana*, 1974, **18**, (1), 3–8

$\text{PtO}_2\cdot 4\text{CaO}$ is formed by the reaction of CaO with PtO_2 or, more slowly, by the reaction of CaO with Pt in the presence of O_2 . Studies of its phases at 293–1473 K enabled them to be identified by X-ray analysis. Oxidation of NH_3 to NO over $\text{PtO}_2\cdot 4\text{CaO}$ indicates that the compound has less catalytic activity than metallic Pt.

Chemisorption of Hydrogen on Platinum Black

A. O. TURAKULOVA, V. S. BORONIN and O. M. POLTORAK, *Vest. Moskov. Univ., Ser. II, Khim.*, 1974, (2), 143–147

Studies of H_2 chemisorption on Pt black over a wide range of temperature and pressure indicated that the technique might be used to determine the degree of Pt dispersion in the catalysts.

Catalytic Oxidation of Hydrogen over Platinum

S. J. GENTRY, J. G. FIRTH and A. JONES, *J. Chem. Soc., Faraday Trans. I*, 1974, **70**, (3), 600–604

The oxidation of H_2 on Pt was studied using a

microcalorimetric technique. The reaction takes place by two mechanisms, depending whether the surface is in an oxidised or reduced state. On the reduced surface, H_2 is dissociatively adsorbed and competes with adsorbed O_2 for adsorption sites. The reaction rate is higher on the oxidised surface where H_2 molecules are weakly adsorbed and react with strongly adsorbed O_2 .

Platinum Catalysts for Exhaust Emission Control: The Mechanism of Catalyst Poisoning by Lead and Phosphorus Compounds

G. J. K. ACRES, B. J. COOPER, E. SHUTT and B. W. MALERBI, *Abstr. Papers, 167th Natl. Mtg., Am. Chem. Soc.*, 1974, (Mar.-Apr.), INDE 90

Studies of the relative toxicity of Pb and P compounds in isolation and in combination are made and the mechanism of Pt catalyst poisoning by Pd and P is compared and contrasted. The relative rates of deactivation by poisoning and other forms of degradation are explored.

The Influence of the Support and the Method of Reduction on the Amount of the Ionic Form of Platinum in Adsorbed Pt Catalysts

Z. V. LUK'YANOVA, T. G. MARTYNYUK, V. I. SHEKHOBALOVA, T. A. POSPELOVA and N. I. KOBOZEV, *Zh. Fiz. Khim.*, 1974, **48**, (4), 928–931

Studies of the Pt(IV) content of Pt catalysts supported on aerosil, SiO_2 , zeolites, $\text{SiO}_2\text{-Al}_2\text{O}_3$, C, WO_3 , and ZnO, with different amounts of Pt, and with various methods of applying and reducing the Pt showed that no Pt(IV) is contained in samples reduced by NaBH_4 or in those prepared on zeolites by ion exchange. On storage the Pt(IV) content begins to increase noticeably after three weeks.

Correlation between the Catalytic Activity and the Surface of Platinum Crystals

G. A. SOMORJAI, *J. Vacuum Sci. Technol.*, 1974, **11**, (1), 250

Several catalytic reactions involving hydrocarbons (*n*-heptane→toluene; cyclohexane→benzene; benzene→cyclohexane) were studied on both low and high Miller index Pt surfaces at 10^{-4} Torr and at 20–450°C using a mass spectrometer. These reactions did not take place on the (111) crystal face but on several stepped crystal faces. Inspection of the surfaces by LEED indicated the formation of ordered carbonaceous surface structures.

Effect of Chlorine on the Dehydrocyclisation of 2-*n*-Butylnaphthalene in the Presence of Palladium/Alumina Catalyst

L. A. ERIVANSKAYA, G. A. SHEVTSOVA and A. F. PLATE, *Neftekhimiya*, 1974, **14**, (3), 373–376

Product ratios from C_8 - and C_9 -dehydrocyclisation of 2-*n*-butylnaphthalene on Pd/ Al_2O_3 and of 1-(naphthyl-2)-butene-1 on Al_2O_3 are related

to the Cl content of the catalysts. On those containing 1.4-1.6 wt.% Cl products of C₅-dehydrocyclisation predominate.

Dehydrogenation of 2-Alkoxy-cyclohexanols

L. ČERVENÝ, A. MARHOUL and V. RŮŽIČKA, *Chem. Průmysl*, 1974, **24**, (4), 187-190

The catalytic dehydrogenation of 2-alkoxy-cyclohexanols to 2-alkoxyphenols was studied in the gaseous phase, 2-methoxy-, 2-ethoxy, and 2-isopropoxy-cyclohexanols being used as model compounds. Best results were obtained using a catalyst of 3% Pd/charcoal, modified by 6% K₂CO₃ applied as an aqueous solution to the reduced catalyst.

Selective Oxidation of Olefins over Noble Metal Catalysts. IV. Oxidative Dehydrogenation of 1-Butene over Platinum Group Metals and Modified Palladium Catalysts. V. Mechanism of Palladium-catalysed Oxychlorination of Propylene

H. TAKASHIMA, K. FUJIMOTO and T. KUNUGI, *Nippon Kagaku Kaishi*, 1974, (3), 428-433, 434-438

Studies of catalysts during oxidative dehydrogenation of 1-butene showed that catalytic activity decreased in the order: Pd > Rh > Pt > Ir > Ru. The effects of additives on Pd catalysis and on the mechanism of oxychlorination of propylene over supported Pd was studied.

Oxidation of Carbon Monoxide on Palladium

R. L. PARK and D. G. SCHREINER, *J. Vacuum Sci. Technol.*, 1974, **11**, (1), 248

The reaction of CO with absorbed O₂ on a Pd surface at room temperature to evolve CO₂ was studied by infrared absorption methods.

Preparing Finely Dispersed Palladium Particles

Y. T. CHEN and S. SRINIVASAN, *Abstr. Papers, 167th Natl. Mtg., Am. Chem. Soc.*, 1974 (Mar.-Apr.), COLL 82

Studies were made to prepare Pd particles with an average diameter <50 Å by using electroless deposition techniques and the effects of stirring, temperature, time of reaction, and surfactant on the morphological characteristics of Pd particles were examined. The results showed that ultrasonic stirring of the solution and temperature of 10°C are the best conditions for a high rate of nucleation.

On the Mechanism of Conversion of Hydrocarbons with Water Vapour on Rhodium/Alumina Catalyst

G. L. RABINOVICH and V. N. MOZHAIKO, *Neftekhimiya*, 1974, **14**, (2), 215-219

The conversion of hydrocarbons with H₂O vapour over Rh/Al₂O₃ includes the adsorption

and activation of H₂O on the hydrophilic surface of the Al₂O₃ support. The activity of Rh/α-Al₂O₃ in toluene dealkylation and in n-heptane conversion with H₂O vapour increases when γ-Al₂O₃ is added to the catalyst.

Asymmetric Ruthenium Catalyst Modified by Optically Active Amino Acids

E. I. KLABUNOVSKII, N. P. SOKOLOVA, V. I. NEUPOKOEV, T. A. ANTONOVA and S. E. TERNOVSKII, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1974, (6), 1361-1364

Studies of the asymmetric hydrogenation of ethyl acetoacetate on skeleton Ru and 5% Ru/SiO₂ catalysts modified by optically active amino acids showed that the greatest yield was obtained using catalyst modified with L-glutamic acid. The yield of ethyl-β-oxybutyrate was related to the pH and temperature of the modified catalyst. Optimum pH is close to the isoelectric point of the amino acids.

Hydrogenation of Carbon Dioxide over a Supported Ruthenium Catalyst

F. L. KESTER, *Abstr. Papers, 167th Natl. Mtg., Am. Chem. Soc.*, 1974, (Mar.-Apr.), FUEL 17

The recent data on reaction rates for the hydrogenation of CO₂ over 0.5% Ru/Al₂O₃ were analysed and interpreted to proceed in steps to CO and then to CH₄. The rate constant and activation energy were given along with adsorption constants for CO, CO₂ and H₂O.

Catalytic Properties of Metal Phosphides.

I. Qualitative Assay of Catalytic Properties

E. L. MUETTERTIES and J. C. SAUER, *J. Am. Chem. Soc.*, 1974, **96**, (11), 3410-3415

Preparation studies of transition metal phosphides/Al₂O₃ and qualitative comparison of these phosphides with Pd, Pt, Rh, Ru showed that with Ru phosphide surfaces, there was a relatively selective interaction of C₂H₂ and H₂ to give C₂H₄.

Recent Developments in Platinum Metal Catalyst Systems

G. J. K. ACRES, A. J. BIRD and P. J. DAVIDSON, *Chem. Engr.*, 1974, (283, March), 145-148, 157

Activity, selectivity and life of Pd, Pt, Ir, Os, Rh, and Ru catalysts were studied during hydrogenation of nitrobenzene at 1 atm, of benzoic acid at 100 atm, of dinitrotoluene at 2-15 atm, and the reactor design for catalytic exhaust emission control was discussed.

HOMOGENEOUS CATALYSIS

Hydrogenation of Unsaturated Hydrocarbons in the Presence of Pt-Sn(II) Complexes

L. KH. FREIDLIN, N. V. BORUNOVA and YA. G. MUKHTAROV, *Neftekhimiya*, 1974, **14**, (2), 171-173

The rate and direction of hydrogenation and of

C=C bond transfer in unsaturated hydrocarbons in the presence of Pt-Sn(II) complexes depends on the structure of the reactants and on the composition of the active complexes. The rate of hydrogenation of allylbenzene and of pentene-1 passes through a maximum when $p_{H_2} = 0.5$ atm. Pt-Sn(II) complexes are most active when Sn/Pt=12. The activity is closely related to the concentration of both components in the solution.

Kinetics and Mechanism of the Homogeneous Hydrogenation of Cyclohexene and of Sulpholene-3 in the Presence of a Reduced $PtCl_2(H_2O)[P(C_6H_5)_3]$ Complex

V. F. ODYAKOV and K. I. MATVEEV, *Kinet. Kataliz.*, 1974, 15, (2), 349-353

The limiting stage in hydrogenation of cyclohexene and of sulpholene-3 in the presence of reduced $PtCl_2(H_2O)[P(C_6H_5)_3]$ is either the formation or the decomposition of Pt alkyl hydride complexes with the formation of saturated compounds. Kinetic studies showed that the constant K_1 of formation of LPt-olefin complexes for sulpholene-3 is less than for cyclohexene despite the greater electronegative nature of the substituents in sulpholene-3.

Organic Synthesis by Means of Noble Metal Compounds. LI. Palladium-catalysed Addition of Butadiene to Nitroalkanes

T. MITSUYASU and J. TSUJI, *Tetrahedron*, 1974, 30, (7), 831-834

Butadiene reacts with nitroalkanes in the presence of PPh_3 complexes of Pd. α -Hydrogen atoms of nitroalkanes are displaced with 2, 7-octadienyl groups to give nitroolefins, which may be reduced to give novel long chain amines having a primary amino group at the middle of the carbon chain.

XCII. Palladium Catalysed Hydrosilylation of Monoenes and Conjugated Dienes

J. TSUJI, M. HARA and K. OHNO, *Tetrahedron*, 1974, 30, (14), 2143-2146

Pd compounds and metallic Pd combined with phosphine are active catalysts for the selective hydrosilylation of terminal olefins. Butadiene and trichlorosilane give a 1:1 adduct, and trimethylsilane gives a 1:2 adduct. Special features of the Pd-catalysed hydrosilylation reactions are discussed.

Palladium-promoted Addition of Amines to Isolated Double Bonds

B. ÅKERMARK, J. E. BÄCKVALL, L. S. HEGEDUS, K. ZETTERBERG, K. SIIRALA-HANSEN and K. SJÖBERG, *J. Organometal. Chem.*, 1974, 72, (1), 127-138

Pd(II) complexes are able to promote amination of terminal olefins, to give, after reduction, high yields of amines. Internal olefins may also be aminated, but with poorer yields; cyclohexene and

cyclooctene react particularly slowly. Means of avoiding formation of bis-(amine)-Pd complexes are discussed. Preliminary mechanistic studies show that three moles of amine are required per mole of Pd to ensure good yields.

An Efficient and Selective Monohydrido Rhodium(I) Homogeneous Hydrogenation Catalyst Containing a Cyclic Phosphine

D. E. BUDD, D. G. HOLAH, A. N. HUGHES and B. C. HUI, *Can. J. Chem.*, 1974, 52, (5), 775-781

The preparation of $RhH(DBP)_4$, DBP being a dibenzophosphole derivative, is described. This Rh complex is a highly effective and selective catalyst for the homogeneous hydrogenation of terminal olefins. Kinetic and mechanistic data for the hydrogenation of 1-hexene are given.

Study of the Reactions of Hydrogenation and Isomerisation of Olefins in the Presence of Catalytic Systems Containing Complexes of Rhodium with Triphenylphosphine and Dimethylsulphoxide

L. KH. FREIDLIN, YU. A. KOPYTTSEV, N. M. NAZAROVA, B. L. LEBEDEVA and B. L. KHUSID, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1974, (6), 1325-1330

The introduction of the DMSO ligand into $(Ph_3P)_3RhCl$ with subsequent treatment by $NaBH_4$ in DMSO solution increases the catalytic activity of the complex for transfer of terminal C=C bonds and for *cis-trans* conversion of β -olefins. Splitting of the olefin chains leads to a reduced rate of isomerisation. The rate of isomerisation sharply rises in the presence of H_2 , indicating the intermediate formation of hydrides.

Investigation of the Rate and Selectivity of Reduction of Alkylcyclohexanones by 2-Propanol in the Presence of Triphenylphosphine Complexes of Ruthenium, Rhodium and Iridium

V. Z. SHARF, L. KH. FREIDLIN, V. N. KRUTII and I. S. SHEKOYAN, *Ibid.*, 1330-1334

The rate and selectivity of reduction of 2-, 3- and 4-alkylcyclohexanones by 2-propanol in the presence of Ru, Rh and Ir complexes depend on the type of metal atom, the connected ligands and the position of the alkyl group. Substitution in position 2 decreases the rate of H transfer. $RhCl(PPh_3)_3$ and $Rh(NO)Cl(PPh_3)_2$ catalyse reduction of 3- and 4-alkylcyclohexanones to form mainly the thermodynamically less stable alkylcyclohexanols while $RuCl_2(PPh_3)_3$, $HRu(CO)Cl(PPh_3)_3$, $Ir(CO)(PPh_3)_2$, $Rh(CO)Cl(PPh_3)_2$, $Rh(Me_2SO)Cl(PPh_3)_2$, and $Rh(OH)(CO)(PPh_3)_2$ direct the process towards forming the thermodynamically more stable alkylcyclohexanols. Those complexes not containing CO groups catalyse reduction of 2-alkylcyclohexanone to form mainly the thermodynamically less stable *cis*-2-alkylcyclohexanol.

Reactive Transition Metal Dinitrosyl Complexes. Synthetic Uses and Catalytic Properties

B. L. HAYMORE and J. A. IBERS, *J. Am. Chem. Soc.*, 1974, **96**, (10), 3325-3327

Series of reactions and experiments of Rh, Ir dinitrosyl complexes showed that they are very reactive and that the conversion of NO and CO into NO₂ and CO₂ is catalytic and general in scope. The reactions implicate transition metal dinitrosyls as the important species in the reduction of NO by CO.

Photochemical Activation of IrCl(CO)(PPh₃)₂ Hydrogenation Catalysts

W. STROHMEIER and G. CSONTOS, *J. Organometal. Chem.*, 1974, **72**, (2), 277-282

Under weak U.V. radiation the activity of IrCl(CO)(PPh₃)₂ as a hydrogenation catalyst is increased approximately fortyfold. Reactive intermediates are formed in both reversible and irreversible steps. Once the active intermediate compound has been produced in the irreversible step, rapid hydrogenation proceeds even in the absence of radiation.

Catalytic Action of Ruthenium Compounds in the Process of Styrene Oxidation

M. E. PUDEL' and Z. K. MAIZUS, *Neftekhimiya*, 1974, **14**, (3), 412-416

RuCl₂(PPh₃)₃ additions catalyse the oxidation of styrene and increase the yield of styrene oxide. The styrene oxide:benzaldehyde concentration ratio rises with increased temperature and decreased O₂ concentration in the oxidising gas.

On the Catalytic Properties of Blue Complexes of Ruthenium

L. KH. FREIDLIN, E. F. LITVIN and K. G. KARIMOV, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1974, (4), 821-824

Blue Ru chloride complexes were produced by reducing Ru(IV) compounds with H₂ in the presence of Ru black. Ru chloride complexes promote C=C bond migration and *cis-trans*

isomerisation of olefins not catalysed in hydrogenation. These complexes catalyse selective hydrogenation and isomerisation of dienes.

Stoichiometric Hydrogenation of Olefins Using HRuCl(PPh₃)₃ and Formation of an *ortho*-Metallated Ruthenium(II) Complex

B. R. JAMES, L. D. MARKHAM and D. K. W. WANG, *J. Chem. Soc., Chem. Commun.*, 1974, (11), 439-440

Studies of stoichiometric hydrogenation of olefins using HRuCl(PPh₃)₃ in the absence of H₂ showed formation of the dimer [(Ph₃P)ClRu(*o*-C₆H₄PPh₂)]₂ which reacted with H₂ and HCl, to yield catalytically important bisphosphine complexes RuXCl(PPh₃)₂ (X=H, Cl).

GLASS TECHNOLOGY

A New Design of Nozzle for Bubbling Glass

T. M. GALIEVA and S. I. MATYUSHA, *StekloKeram.*, 1974, (5), 16-17

The nozzle of the glass bubbling tube is covered with Pt, both in the old design and in the new design, which has wider bores in the corundum twin-channel tubing.

ELECTRICAL AND ELECTRONIC ENGINEERING

Reaction Rates for Pt on GaAs

D. J. COLEMAN, W. R. WISSEMAN and D. W. SHAW, *Appl. Phys. Lett.*, 1974, **24**, (8), 355-357

The rate at which GaAs reacts with Pt was determined at 300-400°C. The amount of GaAs reacted was determined by measurement of the movement of the original Pt Schottky-barrier contact into the GaAs. The amount of GaAs reacted is a function of annealing time at several different temperatures. The reaction follows a parabolic rate law with activation energy of 1.6eV. Some changes in the electrical characteristics of the Schottky barrier are observed.

NEW PATENTS

CHEMICAL COMPOUNDS

Palladium Acetylacetonate of Low Chlorine Content

BAYER A. G. *U.S. Patent* 3,787,462

A high purity Pd acetylacetonate is obtained by precipitating a Pd compound from an aqueous alkali PdCl₂ solution with an alkali metal hydroxide, converting the precipitate to the Pd acetylacetonate with acetylacetone and washing and drying the acetonate.

Compounds of Ruthenium

JOHNSON MATTHEY & CO. LTD.

U.S. Patent 3,793,355

A composition of matter has the general formula MM'M"XA₆LL'L" where M, M' and M" are the same or different transition metals selected from the second or third series of the periodic table; X is O, S, N, P or B; A is an anionic element or group and L, L' or L" are neutral or anionic ligands. A preferred compound is Ru₃O(OCOMe)₆(PPh₃)₃ and generally the Ru carboxylates are used as homogeneous catalysts.