

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

The Homogenisation Quenching of Platinum

A. ČIŽEK, F. PARIŽEK, A. ORLOVÁ and J. TOUŠEK, *Czech. J. Phys., B*, 1970, **20**, (1), 56-62

Black dots $\approx 100\text{\AA}$ diameter were observed during transmission electron microscopy of the defect structures of thin foils prepared from 99.9 and 99.99% Pt samples quenched from 1300°C. The dots are interpreted as vacancy clusters retained in the presence of impurities. They appear to be spherical and $\approx 110\text{\AA}$.

Thermodynamic Properties by Levitation Calorimetry. I. Enthalpy Increments and Heats of Fusion for Copper and Platinum

A. K. CHAUDHURI, D. W. BONNELL, L. A. FORD and J. L. MARGRAVE, *High Temperature Sci*, 1970, **2**, (3), 203-212

Electromagnetic levitation heating and isothermal-drop calorimetry shows that ΔH_{fus} for liquid Pt at 2202-2631K is 5300 ± 150 cal/mole.

Investigation of the Decomposition Kinetics of Gold-Platinum Alloys by Means of Electrical Resistivity

G. KRÁLIK, *Z. Metallkunde*, 1970, **61**, (10), 751-756
Resistivity measurements on 15, 25, 55 and 65 at.% Au-Pt alloys to study decomposition after homogenising and quenching in a salt bath clearly indicated the influence of quenched-in vacancies at the start of ageing. Annealing-out kinetics were explained by migration of divacancies. Migration energies were derived from the decay times of vacancy supersaturation. Spinodal temperatures and atomic diffusion energies were estimated.

Resistance Minimum Phenomena in Exchange Enhanced Pd and Pt Alloys

H. NAGASAWA, *J. Phys. Soc. Japan.*, 1970, **28**, (5), 1171-1180

The magnetic susceptibility and solute resistance of Cr impurity in $\text{Pd}_{1-c}\text{Rh}_c$ ($c=0, 0.01, 0.04, 0.05, 0.08, \text{ and } 0.10$) and also in Pt were measured. The addition of Cr brought about a large increase in the magnetic susceptibility of $\text{Pd}_{1-c}\text{Rh}_c$; below 10K the solute resistivity obeyed a T^2 law. Both effects are explained by the negative polarisation of neighbouring Pd atoms.

Preparation of Homogeneous Palladium-Silver Alloy Films

R. L. MOSS, D. H. THOMAS and L. WHALLEY, *Thin Solid Films*, 1970, **5**, (1), R19-R22

21-68 at.% Pd-Ag films were produced by

simultaneous evaporation at 5×10^6 - 8×10^{10} Torr of Pd and Ag beads previously outgassed on W heating loops. Their good bulk homogeneity was shown by their small lattice constant deviations and symmetrical X-ray diffraction line profiles. The films were relatively unsintered and crystallite size decreased with increasing vacuum.

Low Temperature Heat Capacities of Palladium-Boron Solid Solutions

M. MAHNIG and L. E. TOTH, *Phys. Lett. A*, 1970, **32A**, (5), 319-320

The heat capacities of a series of Pd-B solid solutions were measured at 1.6-10K. Results indicate that the B atoms donate essentially all of their three valency electrons to the d-bands of the metal. The Debye temperature of the system remained roughly constant with electron concentration.

The Thermodynamic Properties of Cobalt-Palladium Solid Solutions

L. R. BIDWELL, F. E. RIZZO and J. V. SMITH, *Acta Metall.*, 1970, **18**, (9), 1013-1019.

The thermodynamic activities of Co-Pd solid solutions relative to pure f.c.c. ferromagnetic Co were measured from 800-1100°C. The activity of Co showed positive departures from ideality in Co-rich alloys, and negative departures in Pd-rich alloys; the activities of Pd showed negative departures at all compositions. Heats of mixing were endothermic for Co-rich compositions and exothermic for Pd-rich compositions. The relative integral molar excess entropies were positive for all compositions. A miscibility gap below 600°C at high Co concentrations is suggested by the experimental results.

Ordered Phase in the Co-Pd Alloy System

Y. MATSUO and F. HAYASHI, *J. Phys. Soc. Japan*, 1970, **28**, (5), 1375

Electron diffraction observations have revealed the existence of a previously unreported ordered state in evaporated films of Co-Pd alloys. The evidence for an order-disorder transformation in CoPd_3 is discussed. The highest temperature of the transformation is $\approx 800^\circ\text{C}$ at 75 at.% Pd.

Antiferromagnetism in Disordered Cr-Pd Alloys

T. KANEKO and H. FUJIMORI, *Ibid.*, 1373

The magnetic properties of disordered 28-34% Cr-Pd alloys were studied at 4.2-300K. Results are presented graphically and include susceptibility-temperature curves and values of the Néel and Curie temperatures. The effective magneton

number $\mu_{\text{eff}}/\text{Cr}$ ion is calculated to lie between 1.7–2.2 μ_{B} and is in inverse position to Cr content. Antiferromagnetism in this system is thought to originate from the antiferromagnetic coupling between the dwarf moments of Cr atoms.

Magnetic Properties of Amorphous Pd-Si Alloys Containing Iron

R. HASEGAWA, *J. Appl. Phys.*, 1970, **41**, (10), 4096–4100

Magnetic properties of amorphous $\text{Fe}_x\text{Pd}_{80-x}\text{Si}_{20}$ alloys ($x=0.5-7.0$) were studied at 1.5–300K in fields up to 8.40 kOe. Above the Debye temperature θ_{d} the alloys are paramagnetic, and below θ_{d} superparamagnetic clusters exist. Ferromagnetism was found in amorphous $\text{Fe}_7\text{Pd}_{73}\text{Si}_{20}$ alloys with a Curie temperature of 28K. Results suggest that the d-d spin exchange interaction is weaker for alloys in the amorphous state than for those in the corresponding crystalline state.

Resistance Anomaly of Dilute Co Impurity in Rh

H. NAGASAWA, *Phys. Lett. A*, 1970, **32A**, (4), 271–272

The resistivity and magnetic susceptibility of dilute Co impurity in Rh were measured at 1.5–300K. Values of observed Co solute resistivities are presented graphically. The residual resistance of the Co is given as 0.34 $\mu\Omega/\text{at.}\%$ Co; the effective magnetic moment is 5.0 $\mu_{\text{B}}/\text{atom Co}$, and the Weiss temperature is $1200 \pm 100\text{K}$.

Some Aspects of Phase Transformations in Near-equiatomic Niobium-Ruthenium Alloys

B. K. DAS, M. A. SCHMERLING and D. S. LIEBERMAN, *Mater. Sci. Engng.*, 1970, **6**, (4), 248–254

Studies of reversible phase transformations in three near-equiatomic Ru-Nb alloys by electrical measurements, hot stage optical metallography, X-ray diffraction and magnetic susceptibility measurements suggested a two-stage mechanism in which on cooling the high temperature cubic β phase transforms to f.c. tetragonal β' phase, which transforms to f.c. orthorhombic β'' phase.

CHEMICAL COMPOUNDS

A Survey of Dinitrogen Complexes of the Transition Metals

J. E. FERGUSSON and J. L. LOVE, *Rev. Pure Appl. Chem.*, 1970, **20**, 33–50

The preparation and properties of dinitrogen complexes of transition metals including Ru, Os, and Ir are surveyed.

Interaction of Ruthenium Trichloride with Zinc

A. N. RYABOV, E. N. RYABOV, G. R. VASILENKO and I. I. KOZHINA, *Vestnik Leningrad Univ., Ser. Fiz. Khim.*, 1970, (10), 98–101

The reduction of $\alpha\text{-RuCl}_3$ by Zn was studied by

means of thermographic and X-ray methods. The reaction goes as follows: $\alpha\text{-RuCl}_3 + \frac{1}{2}\text{Zn} \rightarrow \text{Ru} + \frac{1}{2}\text{ZnCl}_2$. ΔH_{298}° for $\alpha\text{-RuCl}_3$ is 47.4 ± 2.6 kcal/mole.

ELECTROCHEMISTRY

Kinetics of the Chemical Reduction of Platinum Black Surface Oxides

L. D. BURKE and A. MOYNIHAN, *Electrochim. Acta*, 1970, **15**, (9), 1437–1443

The rate at which anodic oxide films of platinised Pt electrodes react with H_2 in aqueous H_3PO_4 was investigated by measuring the amount of oxide film remaining after various reaction times. The reaction rate is inversely proportional to the oxide coverage, probably due to inhibition of oxidation of H_2 by adsorbed oxygen species on the surface. The kinetics of the reaction are given.

A Ring-disc Electrode Study of the Current/Potential Behaviour of Platinum in 1.0M Sulphuric and 0.1M Perchloric Acids

D. C. JOHNSON, D. T. NAPP and S. BRUCKENSTEIN, *Ibid.*, 1493–1509

The production of small amounts of soluble species during oxidation and reduction of a Pt electrode was established using the rotating ring-disk electrode. Pt(II) is produced when an oxidised Pt electrode is reduced, and an unidentified species is produced during oxidation.

Polarisation in Molten Oxides

F. TOUSSAINT, M. BOFFE and E. PLUMAT, *Silicates Ind.*, 1970, **35**, (718), 185–191

Analysis of the intensity-potential curves gave the kinetics of the electrochemical processes at the surface of Pt and simple or complex oxides, e.g. stabilised SnO_2 , ZrO_2 or calcined kaolin in molten oxides. The method of electrical conduction of the electrode determined the interface where the electrochemical reaction took place.

Adsorption of Anions on Smooth Platinum Electrodes

V. S. BAGOTSKII, YU. B. VASILIEV, J. WEBER and J. N. PIRTSKHALAYA, *J. Electroanal. Chem. Interfacial Electrochem.*, 1970, **27**, (1), 31–46

The effect of the adsorption of H_2 , O_2 and CH_3OH on smooth Pt electrodes was investigated. Chemisorbed I^- ions cause an overall decrease in the amount of adsorbed H_2 ; and adsorption of anions lowers that of O_2 and CH_3OH . These effects were used to determine quantitatively the surface coverage with chemisorbed anions.

Hydrogen Adsorption and Methanol Oxidation on Electrolytic Mixed Pt-Rh Deposits

A. M. SKUNDIN, E. K. KHODZHAIEVA and V. S. BAGOTSKII, *Elektrokhimiya*, 1970, **6**, (8), 1133–1135

Differential curves for absorption of H_2 by Pt,

Rh and electrolytic mixed deposits of 2, 12.5, 20, 50 and 75% Rh-Pt, and polarisation curves for the electrooxidation of 1M CH₃OH in 1N H₂SO₄, on Pt, Rh and the mixed deposits of 12.5, 20, 50 and 87.5% Rh-Pt show that the absorption properties of the mixed deposits are similar to those of Rh but that the catalytic properties approximate to those of Pt.

Effect of the Structure of Electrodeposited Platinum on its Adsorptive Properties and Electrocatalytic Activity

O. A. KHAZOVA, YU. B. VASILIEV and V. S. BAGOTSKII, *Ibid.*, (9), 1367-1370

Variations in the catalytic activity of platinised Pt electrodes produced by electrodeposition at various potentials, are connected not with the change in rate constants, as in the case of increased roughness, but with the surface concentration of the reacting substances.

Investigation of Mixed Platinum-Rhodium Electrode-catalysts. Adsorption of Hydrogen on Alloys in Sulphuric Acid Solutions

G. S. MANANKOVA, T. M. GRISHINA, G. P. KHOMCHENKO and G. D. VOVCHEENKO, *Vest. Moskov. Univ., Ser. II, Khim.*, 1970, 25, (4), 427-431

The adsorption of H₂ and the catalytic activity for hydrogenation of acrylic acid in H₂SO₄ solutions using Rh-Pt electrode catalysts are greatest for 48% Rh-Pt. Surface area of these electrode catalysts was measured by charging curves and chromatography. A new method for Rh content in Rh-Pt is suggested.

The Cathodic Evolution of Hydrogen on Ruthenium and Osmium Electrodes

A. R. KUHN and P. M. WRIGHT, *J. Electroanal. Chem. Interfacial Electrochem.*, 1970, 27, (2), 319-323

Current density - potential curves for the H₂ evolution reaction in HCl and NaCl solutions at 25°C on Ru and Os electrodes were obtained at different pH values. Kinetics were determined.

ELECTRODEPOSITION AND SURFACE COATINGS

Structure of Evaporated PtSi on Si

G. A. WALKER, R. C. WNUK and J. E. WOODS, *J. Vacuum Sci. Technol.*, 1970, 7, (5), 543-546

A study of the structure of evaporated or sputtered Pt on Si substrates has conclusively shown that for annealing temperatures up to 700°C the only phases present are Pt and PtSi.

Electrodeposition of Palladium in Amino-hydroxide, Sulphamate, and Bromide Electrolytes

I. F. KUSHEVICH and N. T. KUDRYANTSEV, *Zashchita Metal.*, 1970, 6, (4), 465-469

Electrolytes based on Pd(NH₃)₄(OH)₂,

Pd(SO₃NH₂)₂, [Pd(NH₃)₄](SO₃NH₂)₂, Pd(NH₃)₂(NO₂)₂, K₂PdBr₄, and Pd(NH₃)₄Br₂ were compared. Polarisation curves were obtained at 20°C at different values of pH. Current densities were varied between 0.1 and 0.8 A/dm².

LABORATORY APPARATUS AND TECHNIQUE

Two Methods for the Fabrication of Self-supporting Osmium Targets

R. F. CASTEN, J. S. GREENBERG, G. A. BURGINYON and D. A. BROMLEY, *Nucl. Instrum. Methods*, 1970, 80, (2), 296-298

Thin targets <1000 μg/cm² of self-supporting isotopically enriched Os suitable for use in nuclear reaction and scattering experiments and robust targets of several mg/cm² were fabricated by use of the described apparatus and methods.

JOINING

Braze Alloy Investigation

L. F. JILLY, *NASA Contract Rept. NASA-CR-66845*, 1969, 11 pp

Palniro RE brazing alloy of composition 55 wt.% Au, 30 wt.% Ni, and 15 wt.% Pd with a nominal braze temperature of 1107°C has been developed for use on the Hypersonic Research Engine. The properties of Palniro RE are compared with those of Palniro 1 and 4, which for instance are superior in creep rupture resistance. Although Palniro RE cannot be used at the highest engine temperatures it is suitable, for example, for brazing the manifolds to the shell structure.

HETEROGENEOUS CATALYSIS

Platinum Recovery in Nitric Acid Production

Nitrogen, 1970, (66), 40-42

The three methods of recovering Pt from Pt-Rh gauzes are described. The Degussa process uses a Pd-Au gauze below the catalyst gauze; the OSW process employs CaO below the catalyst gauze; the Hercules-Baker process uses glass fibre or ceramic filters to remove Pt present in the gas stream. The economics of Pt recovery are discussed.

Platinum Dioxide as a Catalyst in the Reaction of Ammonia Oxidation into Nitrogen Oxide during Nitric Acid Production

H. SIKORA, *Chemik*, 1970, 23, (1), 11

PtO₂ catalyses oxidation of NH₃ to N oxides at as low as 300°C without prior activation being necessary, unlike Pt which requires heating to a high temperature with a H₂ burner or by burning C₂H₅OH on its surface to convert it to PtO₂.

Hydrocracking with Chlorinated Platinum-Alumina Catalysts for Liquefied Petroleum Gas Production

J. P. GIANNETTI, H. G. MCILVRIED and R. T. SEBULSKY, *Ind. Engng. Chem., Process Des. Dev.*, 1970, 9, (3), 473-478

Specially chlorinated Pt/Al₂O₃ catalysts were prepared by reacting Pt/Al₂O₃ with HCl gas, then with a S chloride or SO₂ and Cl₂ and finally with HCl again. Pentane, hexane and a pre-treated light naphtha were hydrocracked at 200-290°C, and gave results usually obtained at ~480°C with conventional catalysts.

Chemisorption of Different Gases on Platinum/Alumina Type Catalysts

T. IOST, T. FILOTTO and G. KALMUCHI, *Petrol Gaze*, 1970, 21, (2), 111-116

Chemisorption data from the dehydrogenation of cyclohexane on various Pt/Al₂O₃ catalysts showed that information on the size of Pt crystals, the surface coverage by Pt and H/Pt ratio is not always sufficient to correlate chemisorption characteristics and catalytic activity. Heterogeneity of catalyst surface is calculable from Langmuir, Freundlich or Temkin isotherms, and average heat of chemisorption from the Langmuir isotherm helps clarify the chemisorption mechanism.

Texture Study of Catalysts by Adsorption of Gas. III. Measure of the Adsorption of Hydrogen and Oxygen on Platinum Supported Catalyst

V. BARBAUX, B. ROGER, J.-P. BEAUFILS and J. E. GERMAIN, *J. Chim. Phys.*, 1970, 67, (5), 1035-1040
O₂ and H₂ chemisorption on Pt/Al₂O₃ catalysts were performed in an electronic vacuum microbalance, after in situ outgassing, by the gravimetric method. The weights of gases irreversibly adsorbed at 20°C during a cycle: vacuum, O₂, H₂, vacuum, O₂ agree with: Pt + $\frac{1}{2}$ O₂ = PtO; PtO + $\frac{3}{2}$ H₂ = PtH + H₂O; PtH + $\frac{3}{4}$ O₂ = PtO + $\frac{1}{2}$ H₂O. The metal surface area and intrinsic catalytic activity were calculated.

Selective Catalytic Reduction of Oxides of Nitrogen by Ammonia on a Platinised Catalyst

G. A. SKVORTSOV, A. P. ZASORIN and A. I. PODZHARSKII, *Khim. Promyshlennost*, 1970, (6), 435-437

The process of reduction of N oxides by NH₃ over Pt/Al₂O₃ was studied with regard to effects of temperature, concentration of NH₃ and concentration of O₂.

On the Role of the Support in Platinum/Alumina Catalysts

I. I. LEVITSKII, KH. M. MINACHEV and V. V. VORONIN, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1970, (9), 2007-2011

Comparison of the hydrogenolysis of methyl-

cyclopentane using 5% Pt/Al₂O₃ with earlier work showed sharp differences from tests with 0.3% Pt/Al₂O₃. Pt/C and SiO₂ also gave less hydrogenolysis. Al₂O₃ as the support guarantees high dispersion of the supported metal and determines the catalytic properties, presumably due to the different electrical state of the atoms adjoining the support surfaces.

Disproportionation of Cyclohexene and Crossed Disproportionation on Platinum/Alumina

R. MAUREL and G. LECLERCQ, *C.R., Sér. C*, 1970, 271, (4), 239-241

The disproportionation of cyclohexene to cyclohexane in benzene in contact with Pt/Al₂O₃ at 116°C is a complex reaction in which dehydrogenation in benzene precedes hydrogenation.

Kinetics of Consecutive Heterogeneous Catalytic Reaction: Gas-phase Hydrogenation of Phenol on a Platinum Catalyst

V. HANCIL and L. BERANEK, *Chem. Engng. Sci.*, 1970, 25, (7), 1121-1126

The kinetics of consecutive hydrogenation of phenol to cyclohexanol via cyclohexanone on a Pt/SiO₂ catalyst at 150°C were studied. The course of the overall reaction can be described by Langmuir-Hinshelwood type rate equations, which suggests that both composing reactions occur on the same sites of the catalytic surface.

On the Slow Uptake of Hydrogen by Platinised Carbon

M. BOUDART, A. W. ALDAG and M. A. VANNICE, *J. Catalysis*, 1970, 18, (1), 46-51

Burning off the C contaminating the Pt surface of Pt/C before adsorption measurements decreases or suppresses uptake of H₂. C contamination of Pt appears to provide bridges which allow surface diffusion of H atoms from Pt to the C support.

Catalytic Activity of Platinum Catalyst on Polymeric Supports

S. G. FEDORKINA, G. I. EMEL'YANOVA and N. I. KOBOZEV, *Vest. Moskov. Univ., Ser. II, Khim.*, 1970, 25, (3), 350-352

Studies of the adsorption properties of Pt/polymer catalysts showed no noticeable effect of the polymers on the catalytic activity of the Pt. Adsorption capacity of an Al₂O₃ support was increased by polymer coating. Polymers tested were caprone, polycarbonate and the copolymer of phenolphthalein and terephthalic acid.

Palladium: Preparation and Catalytic Properties of Particles of Uniform Size

J. TURKEYICH and G. KIM, *Science*, 1970, 169, (3948), 873-879

Uniform particles of Pd, diameter 55-450Å were prepared by the hydrothermal treatment of

$\text{Al}_2(\text{OH})_3$ sol to form rods of Al_2O_3 on which Pd was adsorbed from aqueous suspension. The activity and kinetics of C_2H_4 hydrogenation on this catalyst were examined.

Effect of Zinc Cations on the Selectivity of Palladium Catalysts on Supports during the Hydrogenation of Dimethylethynylcarbinols

V. A. NAIDIN, G. D. ZAKUMBAEVA and D. V. SOKOL'SKII, *Kinet. Kataliz*, 1970, **11**, (4), 1072-1074

Studies of the effects of adding Zn cations as ZnSO_4 to stationary Pd catalysts for hydrogenation of aqueous solutions of 5-75% dimethylethynylcarbinols showed that the modification causes a sharply increased yield (98%) of dimethylvinylcarbinols.

Liquid-phase Hydrogenation of Heptene-1 on Palladium and Platinum-Palladium Catalysts on Alumina

D. V. SOKOL'SKII, M. I. GORYAEV, G. A. SAVEL'EVA, N. M. POPOVA and A. D. DEMBITSKII, *Neftekhimiya*, 1970, **10**, (4), 489-493

Studies of the liquid-phase hydrogenation of 1- C_7H_{14} in 96% $\text{C}_2\text{H}_5\text{OH}$ at 20°C over Pd/ Al_2O_3 and Pt-Pd/ Al_2O_3 , in relation to catalyst metal content and to the composition of the active phases, showed that it occurs at the expense of weakly bonded H and is accompanied by isomerisation to *cis*- and *trans*-2- C_7H_{14} and 3- C_7H_{14} . Maximum yields on 4% metal/ Al_2O_3 occurs with Pd. Yield decreases as Pt content increases.

X-Ray Studies on Supported Palladium Catalysts

M. UEHARA and S. SUZUKI, *Kogyo Kagaku Zasshi*, 1970, **73**, (5), 852-855

Absorbed amounts of H_2 are proportional to the increase in lattice constant caused by the dissolved H_2 . Dehydrogenation of *n*- C_6H_{10} on Pd/C was investigated, also the α -B phase transition in Pd/C which occurred under a wide range of conditions. The lattice constant of 3.97Å suggested a new type of solid solution of H_2 and Pd.

Hydrogen Absorption Isotherm of Supported Palladium Catalysts

Ibid., 855-859

H_2 absorption isotherms of various supported Pd catalysts were studied and fall into 3 types: (i) perfect step type, in which the Pd exists as uniform crystallites, (ii) imperfect step type, in which the Pd occurs as continuously size-distributed crystallites, (iii) non-step type, Pd as non-crystalline particles. They tend towards the non-step type with increasing specific surface area.

Activity of Various Types of Palladium Catalysts Supported on Polyacrylonitrile

O. A. TYURENKOVA and L. A. CHIMAROVA, *Zh. Fiz. Khim.*, 1970, **44**, (9), 2278-2282

Potentiometric studies of the activity of Pd/poly-

acrylonitrile catalysts in relation to the conditions of Pd reduction show that those reduced in alcoholic media are more active and stable for the hydrogenation of dimethylethynylcarbinols, whereas those produced using dioxane have little activity. Optimum reduction occurs at 40°C but catalyst produced in those conditions is less selective for hydrogenation of dimethylethynylcarbinol.

Investigation of the Step Mechanism and Selectivity of Reduction of Aceto- and Propiophenone on Rh- Al_2O_3

L. KH. FREDLIN, N. V. BORUNOVA, L. I. GVINTER, S. S. DANIELOVA and R. N. BADA KH, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1970, (8), 1797-1803

Rh/ Al_2O_3 catalyses addition of H_2 to aliphatic-aromatic ketones to form alkylphenylcarbinols and alkylcyclohexylketones, depending on the availability of CO groups for hydrogenation. Further reduction depends on the likelihood of either hydrogenolysis of C-OH bonds or of hydrogenation of alkylphenylcarbinol aromatic rings. In mild conditions the former predominates but in severe conditions the latter, forming mainly alkylcyclohexylcarbinols. Partial poisoning of Rh/ Al_2O_3 by Cd showed that reduction of the aromatic rings occurs at various parts of the catalyst surface at various rates unrelated to the process conditions.

Mixed Adsorption Catalysts for Hydrogenation. XVI. Rhodium-Platinum and Rhodium-Palladium Catalysts on Silica Gel

A. A. ALCHUDZHAN, N. Z. EDIGARYAN and M. A. MANTIKYAN, *Arm. Khim. Zh.*, 1970, **23**, (1), 3-8

0.5 wt.% Rh/ SiO_2 catalysts with additions of Pt and Pd were compared with Rh/ SiO_2 , Pt/ SiO_2 and Pd/ SiO_2 catalysts for hydrogenation of C_6H_6 at 90°C, volume ratio $\text{H}_2:\text{C}_6\text{H}_6=4:1$, H_2 gas flow 1.5-2.5 l/h, activity being expressed as % conversion to cyclohexane. Activity increased proportional to Pt content. Activity of concurrently deposited Rh-Pt/ SiO_2 was greater than the total activity of Rh/ SiO_2 and Pt/ SiO_2 catalysts with the same total content of metals. Pd additions tended to decrease catalytic activity, possibly due to its different electronic structure or to an effect of the SiO_2 .

The Hydrogenation of Alkadienes. Part IV. The Reaction of Buta-1,3-diene with Deuterium Catalysed by Rhodium, Palladium, and Platinum

A. J. BATES, Z. K. LESZCZYNSKI, J. J. PHILLIPSON, P. B. WELLS, and G. R. WILSON, *J. Chem. Soc., A, Inorg. Phys. Theor.*, 1970, (14), 2435-2441

Reactions of buta-1,3-diene with Rh/ Al_2O_3 , Pd/ Al_2O_3 and Pt/ Al_2O_3 as catalysts were studied. Butene isomerisation occurs only after desorption although absorbed butyl groups were formed at the Rh and Pt surfaces.

Part V. The Hydrogenation of *trans*- and *cis*-Penta-1,3-diene catalysed by Cobalt, Nickel, Copper, Palladium and Platinum

P. B. WELLS and G. R. WILSON, *Ibid.*, 2442-2447

Gas phase hydrogenation of the pentadienes was investigated using Pd/Al₂O₃ and Pt/Al₂O₃ catalysts amongst others. The reaction was relatively slow; all isomers of *n*-pentene were formed with little or no pentane.

Measurements of Active Site Concentrations at Rhodium, Osmium, Iridium, and Platinum Surfaces by 1,1-Diphenyl-2-picrylhydrazine Oxidation in the Liquid Phase, and Carbon Monoxide Chemisorption from the Gas Phase

R. B. MOYES, P. B. WELLS, K. BARON, K. COMPSON, J. GRANT and R. HESELDEN, *J. Catalysis*, 1970, 18, (2), 224-227

O atoms chemisorbed at the surface of pre-reduced Rh, Ir and Pt powders with diphenylpicrylhydrazine to yield H₂O and the stable diphenylpicrylhydrazyl free radical. The number of active sites present per gram of powder was calculated from concordance determinations of the free radical concentration by e.s.r. and optical spectroscopy.

Hydrogenolysis of Cyclobutane Hydrocarbons on Platinum, Palladium, Rhodium, and Iridium Catalysts

M. YU. LUKINA, T. G. OLFER'EVA, O. V. BRAGIN, A. L. LIBERMAN and B. A. KAZANSKII, *Dokl. Akad. Nauk S.S.S.R.*, 1970, 193, (1), 106-109

Hydrogenolyses of ethylcyclobutane and of other cyclobutane derivatives over Pt/C, Pd/C, Rh/C and Ir/C was studied in constant flow and pulsed flow conditions. With Pt/C and Pd/C the principal products were *n*-hexane and 3-methylpentane. With Rh/C and Ir/C there were also quantities of other pentanes and lower alkanes.

HOMOGENEOUS CATALYSIS

Production of Linear Acids or Esters by the Platinum-Tin Catalysed Carbonylation of Olefins

L. J. KEHOE and R. A. SCHELL, *J. Org. Chem.*, 1970, 35, (8), 2846-2848

A H₂PtCl₆-SnCl₂ couple was used to catalyse the carbonylation of olefins such as dodecene-1 in the presence of methanol to linear esters in 1h at 200 atm.; in the presence of water, acids are formed. K₂PtCl₆ with SnCl₂ also showed reactivity.

The Palladium(II) Chloride and Copper(II) Chloride Catalysed Oxychlorination of Ethylene to Ethylene Chlorhydrin

H. STANGL and R. JIRA, *Tetrahedron Letters*, 1970, (41), 3589-3592

The reaction of C₂H₄ with O₂ in the presence of

PdCl₂-CuCl₂ to produce HO-CH₂-CH₂-Cl is discussed.

Aromatic Substitution of Olefins. The Reaction of Ferrocene with Styrene in the Presence of Palladium(II) Acetate

R. ASANO, I. MORITANI, Y. FUJIWARA and S. TERANISHI, *J. Chem. Soc., D, Chem. Commun.*, 1970, (20), 1293

An example of a very convenient direct synthesis of alkenylferrocenes is the reaction of ferrocene with styrene to produce *trans*- α -styrylferrocene in the presence of Pd(OAc)₂.

Activation of Molecular Oxygen, Hydrogen, Carbon Monoxide, and Olefins by a Rhodium(I) Complex in Nonaqueous Media

B. R. JAMES and F. T. NG, *Ibid.*, (15), 908-909

The complex [(C₆H₁₄)₂RhCl₂]₂, dissolved in dimethylacetamide containing LiCl, reacts with O₂, H₂, CO and some olefins, e.g., maleic acid (MA) to give complexes such as Rh(I)(MA) which have catalytic properties.

Dimeric Metal Acetates for the Homogeneous Hydrogenation of Olefins

B. C. HUI and G. L. REMPEL, *Ibid.*, (18), 1195-1196
Rh₂(OCOME)₄ and Ru₂(OCOME)₄ were shown to catalyse hydrogenation of various olefins in a number of organic solvents.

Homogeneous Catalytic Hydrogenation of Organic Compounds using Rhodiumtriarylphosphine Complexes

J. L. PARSONS, *Diss. Abstr. B*, 1970, 30, (9), 4057
Trichlorotris(4-biphenyl-1-naphthylphenylphosphine)rhodium(III) has been developed as a homogeneous hydrogenation catalyst and has been used for the catalytic reduction of α , β -unsaturated acids and esters. It is superior in performance to other Rh(III) phosphine complexes.

Oxidation by Transition Metal Complexes. I. Oxidation of Styrene and Triphenylphosphine Catalysed by O₂-Ir Complex

K. TAKAO, Y. FUJIWARA, T. IMANAKA and S. TERANISHI, *Bull. Chem. Soc. Japan*, 1970, 43, (4), 1153-1157

The oxidation reactions of styrene and PPh₃ catalysed by various Ir complexes were studied. The complexes IrX(CO)(PPh₃)₂ and Ir[(Ph₂CH₂CH₂Ph)₂Cl] were effective oxidation catalysts. Oxidation with Pd salts was compared with the Ir complexes.

On the Catalytic Decomposition of Perchloric Acid in the Presence of Complex Compounds of Iridium

S. I. GINZBURG and M. I. YUZ'KO, *Zh. Neorg. Khim.*, 1970, 15, (9), 2441-2444

Ir complexes catalyse decomposition of HClO₄

in the presence of H_2SO_4 at 197–200°C. The formation of polymeric Ir(IV) compounds reduces the catalytic activity. Unstable intermediate compounds, probably of Ir(VI), form initially and are strongly oxidising. Small amounts of Ir evaporate during oxidation of Ir perchlorate due to formation of the higher oxide IrO_3 .

Catalytic Oxidation of Triphenylphosphine Using a Ruthenium-Oxygen Complex

B. W. GRAHAM, K. R. LAING, C. J. O'CONNOR and W. R. ROPER, *J. Chem. Soc., D, Chem. Commun.*, 1970, (19), 1272

$Ru(O_2)(NCS)(NO)(PPh_3)_2$ efficiently catalyses oxidation by O_2 of PPh_3 to the oxide.

Hydrogenation of Olefins by μ -Dichloro- π -benzene-ruthenium(II)

I. OGATA, R. IWATA and Y. IKEDA, *Tetrahedron Letters*, 1970, (34), 3011–3014

The hydrogenation of pentenes by $[Ru(C_6H_6)Cl_2]_n$ was studied in various solvents. The catalytic activity and reaction products depended on the solvent used. The mechanism of hydrogenation and the species produced in coordinating solvents, e.g. DMSO, are discussed.

FUEL CELLS

A Fuel-Cell that Operates on Human Blood

Chemical Week, 1970, 107, (2), 40

A fuel cell which could power an artificial heart has electrodes of a noble metal substrate to which selective catalysts of Au-Pd alloys are bonded. Placed directly in the blood, one electrode reacts preferentially with glucose in the blood, the other with O_2 . 20 $\mu w/cm^2$ of electrode

were obtained; about 10 w would be needed to power an artificial heart.

CHEMICAL TECHNOLOGY

Influence of Palladium on the Corrosion and Electrochemical Behaviour of Steel OX25H6T

N. D. TOMASHOV, G. P. CHERNOVA, L. N. VOLKOV, *Zaschita Metal.*, 1970, 6, (4), 425–427

Studies on the steel OX25H6T, which contains 6% Ni and 25% Cr, showed that passivation using 0.1–0.5% Pd occurs in two stages. The corrosion rates for various Pd additions were: 0.1% Pd, 26.8 g/m^2h ; 0.2% Pd, 18 g/m^2h ; 0.5% Pd, 24.5 g/m^2h , in 20% H_2SO_4 at 100°C for 5 h testing.

TEMPERATURE MEASUREMENT

On the Control of the Temperature Regime of Glass Masses Delivered for Moulding

V. M. BUDOV, YU. V. SESKUTOV, V. SH. YAKUPOV, V. S. PAVLOV and V. V. FOKIN, *Steklo Keram.*, 1970, (8), 6–8

Studies of the variations with depth of temperature of molten sheet glass in cooling tanks were carried out using high temperature thermocouples above the surface, Pt-cased thermocouples projecting from the tank walls into the glass and open junction low-inertia Pt:Rh-Pt thermocouples dipped into the glass to various depths. Fluctuations and variations at these points indicate that one temperature-measuring point is insufficient and that the thermal processes are complex.

NEW PATENTS

METALS AND ALLOYS

Alloys of Variable Transition Temperature

F. E. WANG & W. J. BUEHLER
British Patent 1,202,404

The alloy JL_xM_{1-x} has a martensitic transition temperature depending on the ratio L : M. J is a Group VIA metal, and makes up 50 at.% of the alloy, the remaining 50% being L + M, where x is greater than 0 and less than 1. Typically, J is Zr, L is Rh and M is Ru or J is Zr, L is Pd and M is Rh.

Workable Duplex Structured Ruthenium Alloys

INTERNATIONAL NICKEL CO. INC.
U.S. Patent 3,498,763

A cold-workable Ru alloy capable of being cold

drawn to wire contains about 60–90% Ru, 5–40% Cu, up to about 35% Pd and up to 10% Ni. It is produced by liquid-phase sintering, preferably by infiltration of Cu or Cu alloy, into a Ru compact at a temperature between 1083°C and 1500°C.

Dispersion-hardened Noble Metals

P. R. MALLORY & CO. INC. *U.S. Patent* 3,515,542
Cu, Au, Ag, Pt, Pd and their alloys are strengthened or hardened by introducing up to 10% of a compound of Cr, Ti, Th, U, Zr, B or Si or alloys thereof. A melt is formed of the noble metal and the hardening element and gas bubbled through the melt to form the compound, usually an oxide.

Hardening of Platinum Metals

JOHNSON, MATTHEY & CO. LTD
German Appl. 1,533,275

Pt, Pd, Rh and their alloys with one or more