

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Wire of Chemically Pure Platinum Grades PLO-A and PLZ-A. Quality Requirements for Certified Products

U.S.S.R. Std. GOST 5. 1078-71

This Russian standard specifies the limits of diameter, purity of Pt, methods of packing and labelling for transport, and duration of guarantee for certification of Pt wire of the grades mentioned.

Enthalpy and Derived Thermodynamic Functions of Platinum and a Platinum+Rhodium Alloy from 400 to 1700°K

A. C. MACLEOD, *J. Chem. Thermodyn.*, 1972, 4, (3), 391-399

Revised values of the enthalpies of pure Pt and 10 wt.% Rh-Pt from 400-1700K and molar thermodynamic properties of Pt from 300-2000K are given. It is suggested that the high temperature properties of Rh require redetermination.

Physical Characteristics of Electrodeposited Finely Divided Platinum-Cobalt Alloys

A. I. ZAYATS, A. A. PAVLYUKOV and N. A. PEREKHREST, *Porosh. Met.*, 1972, 12, (4), 7-11

Pt-Co alloy powder was electrodeposited from a solution of constant Pt and Co ion concentration. The structure and coercive force of the alloy depended on its Pt content; its dispersion was unaffected by electrolysis conditions.

Features of the Fine Structure and Magnetic Properties of Iron-Platinum Alloys with 32 and 35 at.%Pt

E. N. VLASOVA, V. I. GORBUNOV, I. A. KOMAROVA and T. P. SAPOZHKOVA, *Fiz. Metal. Metalloved.*, 1972, 34, (5), 959-965

Monocrystals of 32 and 35 at.% Pt-Fe were studied by X-rays in the equilibrium and high coercivity states, and during isothermal annealing. The change in magnetic saturation and in coercive force during annealing at 750°C was also studied. Relation of structural changes to magnetic properties led to conclusions as to the structural features responsible for the high coercive force.

Effect of Plastic Deformation on the Structural Composition and Coercive Force of Some High Coercivity Alloys

G. V. IVANOVA, N. N. SHCHEGOLEVA, L. M. MAGAT and YA. S. SHUR, *Fiz. Metal. Metalloved.*, 1972, 34, (5), 1014-1021

X-ray and electron microscopy studies of the

effect of plastic deformation on the structure and coercive force of ordered FePt, FePd and CoPt show that deformation induces partial heterogeneity together with breakdown of lamellar domains with double orientation. The coercive force is related to the stage of plastic deformation according to these factors.

Preparation, Single Crystal Growth, and Characterisation of PtSi and PtGe

R. J. BAUGHMAN and R. K. QUINN, *Mater. Res. Bull.*, 1972, 7, (10), 1035-1040

Large polycrystalline ingots of PtSi and PtGe were prepared by lowering a coiled 99.999% pure Pt wire into molten Si or Ge at a controlled rate under an Ar atmosphere. Single crystals up to 1.8×3.5 cm were then grown. Both materials show diamagnetism and good electrical conductivity; their bulk densities and Seebeck coefficients are also reported.

Superconductivity in the Palladium-Hydrogen and the Palladium-Deuterium Systems

B. STRITZKER and W. BUCKEL, *Z. Physik*, 1972, 257, (1), 1-8

Superconducting transitions were observed in the Pd-H and Pd-D systems up to 9K and 11K, respectively. The high concentrations necessary for superconductivity are obtained by implanting H or D ions into the Pd at $T_{\text{liq. He}}$.

Lattice Spacings and Magnetic Susceptibilities of Palladium-Lanthanum, Palladium-Cerium and Palladium-Praseodymium Alloys

J. D. SPEIGHT, *J. Less-common Metals*, 1973, 30, (1), 159-163

Lattice constants and magnetic susceptibilities of rapidly quenched 1-4 at.% La-Pd and Pr-Pd and of 2-8 at.% Ce-Pd alloys were measured. Results suggested that the 4f states in Ce in solid solution in α -Pd are not occupied, the effective valency then being four.

The Alloys of Palladium with Yttrium, Samarium, Gadolinium, Dysprosium, Holmium and Erbium

O. LOEBICH and E. RAUB, *J. Less-common Metals*, 1973, 30, (1), 47-62

Phase diagrams of Pd-Ln alloys were determined by D.T.A., X-ray diffraction and metallographic techniques. In general seven phases occurred: LnPd_3 , Ln_4Pd_5 and LnPd (and Ln_3Pd_2 when $\text{Ln}=\text{Y, Dy, Er}$), all melting congruently; and

Ln_3Pd_2 , Ln_2Pd_3 and LnPd_2 (and Ln_5Pd_2 when $\text{Ln} = \text{Sm, Gd, Ho}$), formed by peritectic reactions. Structural data are given for LnPd_3 , LnPd , Ln_3Pd_2 and Ln_5Pd_2 .

Excess Specific Heat of a Glassy $\text{Pd}_{0.775}\text{Cu}_{0.06}\text{Si}_{0.165}$ Alloy at Low Temperature

H. S. CHEN and W. H. HAEMMERLE, *J. Non-cryst. Solids*, 1972, **11**, (2), 161-169

The specific heat of $\text{Pd}_{0.775}\text{Cu}_{0.06}\text{Si}_{0.165}$ was measured at 2.0-18.0 K. The electronic specific heat of the glassy phase is much smaller than the value calculated assuming the electrons to be free, suggesting a strong association between Pd and Si and a high degree of short range order. The glassy phase has a greater specific heat than the crystalline phase, very similar in position and magnitude to the excess shown at low temperatures by other glass-forming solids.

The Electrical Resistivity of Iridium at High Temperatures

R. T. WIMBER and J. J. HALVORSON, *J. Mater.*, 1972, **7**, (4), 564-567

The electrical resistivity of Ir was measured in the range 293-2275K and an expression was derived to T^4 . Values for the temperature coefficient of resistivity are given.

On the Constitution of the Rhodium-Lead System

M. EL-BORAGY, K. C. JAIN, H. W. MAYER and K. SCHUBERT, *Z. Metallkunde*, 1972, **63**, (11), 751-753

The phase diagram of the Rh-Pb system and lattice parameters of several of its crystal structures were determined. Stability of the phases is discussed.

On the Tensile Properties of Recrystallised Molybdenum Wire Alloyed with Ru and C

N. ARITOMI and H. MIKIDA, *J. Japan Inst. Metals*, 1973, **37**, (1), 127-134

The modification of the tensile properties of recrystallised 0.02 wt.% C-Mo by 0.14 wt.% Ru was investigated. Ru increases strain-hardening but decreases hardness and yield strength at room temperature, thus increasing ductility; it increases yield strength at high temperatures and decreases temperature- and strain-rate-dependence. Ru increases the uniform elongation and "working range" at room temperature.

The Ru-Y Constitution Diagram

E. M. SAVITSKII, V. P. POLYAKOVA and N. R. ROSHAN, *Izv. Akad. Nauk S.S.S.R., Metall.*, 1972, (5), 129-132

Physical and chemical methods were used to construct the constitution diagram of the Ru-Y system and measurements of the alloy properties confirmed the limits of the phases in the system.

Phase Equilibria in the System Ruthenium-Titanium-Hafnium

D. D. GULAMOVA, M. V. RAEVSKAYA and E. M. SOKOLOVSKAYA, *Vest. Moskov. Univ., Ser. II, Khim.*, 1972, (5), 546-550

The complete phase diagram is established for the Ru-Ti-Hf system.

CHEMICAL COMPOUNDS

How to Buy Platinum Group Metals Chemicals

D. LUNING, *Chem. Engng.*, 1972, **79**, (28, Dec. 11), 114, 116, 118

Factors peculiar to the procurement of Pt group metal compounds are discussed, including quality, economic and delivery considerations.

The Electrical Conductivity Behaviour of $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}\cdot 2.3\text{H}_2\text{O}$ at High Pressures

L. V. INTERRANTE and F. P. BUNDY, *Solid State Commun.*, 1972, **11**, (12), 1641-1645

$\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}\cdot 2.3\text{H}_2\text{O}$ was studied at up to 100,000 atm using X-ray and conductivity methods. Changes in conductivity are interpreted in terms of the effect of pressure on the interatomic distance and are discussed in the context of the electronic structure of this material.

Effect of *cis*-Dichlorodiammineplatinum(II) on Cytological and Morphological Changes in Bone Marrow of Mice. Long-term Observations

M. ŽÁK, J. DROBNÍK and Z. REŽNÝ, *Neoplasma*, 1972, **19**, (4), 305-310

After an intraperitoneal injection of 8 mg/kg *cis*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, cell count, mitotic index and relative frequency of individual elements in the bone marrow of mice followed decreasing oscillatory patterns with normalisation within 28 days.

Effect of *cis*-Platinous Diamminodichloride on Graft Rejection. Prolonged Survival of Skin Grafts against H_2 Histocompatibility

A. KHAN, A. ALBAYRAK and J. M. HILL, *Proc. Soc. Exp. Biol. Med.*, 1972, **141**, (1), 7-9

Maximum suppression of skin graft rejection in mice by *cis*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ is achieved by a single injection of 8 mg/kg body weight on the day of transplantation.

Synthesis and Distribution of a Radio-labelled Anti-tumour Agent: *cis*-Diamminodichloroplatinum(II)

R. C. LANGE, R. P. SPENCER and H. C. HARDER, *J. Nucl. Med.*, 1972, **13**, (5), 328-330

The antitumour compound, *cis*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, was synthesised from metastable ^{193}Pt ; its structure was verified by chemical and biological methods. Following i.v. injection into rabbits

there was widespread distribution then accumulation of radioactivity in the kidneys, liver and bladder. Radioactivity remained high in the blood but was low in the brain. Mice showed the same pattern with rapid excretion of the radio-label.

Chemistry of Complexes Related to *cis*-Dichlorodiammineplatinum(II) Anti-tumour Drug

A. J. THOMSON, R. J. P. WILLIAMS and S. RESLOVA, *Struct. Bonding (Berlin)*, 1972, **11**, 1-46

An extensive review of complexes related to *cis*-Pt(NH₃)₂Cl₂ is presented. Their chemistry, photochemistry, physico-chemical properties and biological interactions are discussed and related to their potential in the elucidation of causes and cure of cancer.

Hydroxy Complexes of Platinum(II) and Palladium(II)

G. W. BUSHNELL, K. R. DIXON, R. G. HUNTER and J. J. MCFARLAND, *Can. J. Chem.*, 1972, **50**, (22), 3694-3699

The preparation and structure of the hydroxy-bridged complexes [M₂(OH)₂L₄][BF₄]₂, where M=Pt and L=triethylphosphine, triphenylphosphine or pyridine, or where M=Pd and L=triphenylphosphine, are described. These complexes are stable and resist bridge cleavage by tertiary phosphines under conditions which easily cleave analogous chloro-bridged complexes.

A Superconducting Ternary Sulphide Ag₂Pd₃S

H. R. KHAN, H. TRUNK, C. J. RAUB, W. A. FERTIG and A. C. LAWSON, *J. Less-common Metals*, 1973, **30**, (1), 167-168

Only one intermetallic compound, Ag₂Pd₃S, was found to exist in the Ag-Pd-S system; it has a β-Mn(A-13)-type structure. It is the first ternary Ag-Pd compound observed to be superconducting and undergoes a sharp transition at 1.13K. It is suggested that it may undergo a metal-semiconductor phase transition >300K.

ELECTROCHEMISTRY

A Rechargeable Hydrogen Permeable Palladium Electrode

T. SHIROGAMI, *Extended Abstr., 142nd Natl. Mtg., Electrochem. Soc.*, 1972, **72-2**, 56-57, abstr. 21

H₂ was adsorbed on the palladised surface of a Pd black/Pd foil/Pd,Pt blacks electrode and diffused through the membrane to the KOH electrolyte where it was anodised to H₂O. Up to 600 mA/cm² at 100mV overpotential was obtained. Cathodic polarisation fully reversed the process, producing H₂ at up to 10 atm and 300 mA/cm².

Polarisation Characteristics of an Iridium Electrode

T. OKAMURA, *Denki Kagaku*, 1972, **40**, (11), 796-799

The electrochemical properties of Ir were studied in 1N H₂SO₄, 0.1N NaOH and 5M NaCl. An oxide layer, less stable than that of Rh, forms in both acidic and alkaline solutions but is reduced at almost the same potential as that of formation. The very low chlorine overvoltage of an Ir electrode makes it suitable for use as a brine electrolysis anode, but a small amount of contamination of the Cl₂ with O₂ may be expected.

ELECTRODEPOSITION AND SURFACE COATINGS

Metallising Nonconductors. VI. Vapour Plating

E. GROSHART, *Metal Finish.*, 1972, **70**, (8), 49-51, 54

Very thick, pure deposits of Pt on nonmetal substrates may be obtained by the vapour deposition process. Pt salts of carbonyl-chloride or acetylacetonate are thermally decomposed on the heated substrate. Seamless Pt tubing can be produced by the process, using a C rod as the substrate, which is later removed.

Electrodeposition of Dispersed Platinum-Cobalt Alloys

A. I. ZAYATS and N. A. PEREKHREST, *Zh. Prikladnoi Khim.*, 1972, **45**, (10), 2248-2252

Pt-Co deposits can be obtained from both acidic and alkaline electrolytes. Nearly equiatomic Pt-Co deposits can be obtained from ammine electrolytes under optimum conditions.

Electroless Metal Deposition on Hydrophobic Surfaces

W. P. TOWNSEND, J. A. EMERSON and J. T. KENNEY, *Extended Abstr., 142nd Natl. Mtg., Electrochem. Soc.*, 1972, **72-2**, 530-531, abstr. 216

Polyimide, polyester, epoxy resin, PTFE, PE and PP were uniformly metallised using a Sn(II) electroless process after immersion in a colloidal sensitising dispersion to render them hydrophilic. No other pretreatment was necessary. Sn(II) was deposited and then used to deposit Pd(o) by reduction of Pd(II) in acid solution. Pd(o) is catalytic to electroless metal deposition. Selective UV oxidation of Sn(II) prevented Pd deposition on exposed areas.

Investigation of the Electrodeposition and Some Physical Properties of Dispersed Palladium-Cobalt Alloys

A. I. ZAYATS and V. A. SOBKEVICH, *Zh. Prikladnoi Khim.*, 1972, **45**, (9), 1948-1953

Properties of Pd-Co electrodeposits depend on the conditions of electrolysis. Dispersion of Pd-Co

powders rises with increased current density and decreased temperature and metals concentration. Alloy structure depends upon alloy content. Coercivity of the alloys also rises with increased current density and decreased temperature and metals concentration.

Comparison of Ratings of Sulphate, Nitroschloride and Sulphamine Electrolytes for Ruthenation

N. M. SHMELEVA, A. L. ROTINYAN, P. M. VYACHESLAVOV and E. P. LEONENKO, *Zh. Prikladnoi Khim.*, 1972, **45**, (8), 1728-1733

Studies of sulphate, nitroschloride and sulphamine electrolytes prepared from Ru hydroxychloride showed that the easiest to prepare and adjust to deposit Ru are the sulphamine electrolytes, which give the thickest deposits with the least internal stress. The deposits depend upon the electrolyte composition and process regime. Deposits of Ru on Ni are stable after preliminary degreasing of Ni in organic solvent and electrochemically in alkaline solution, followed by electrochemical activation.

LABORATORY APPARATUS AND TECHNIQUE

Separation of ^1H and ^3H on a Palladium Filter

V. V. ISHUTIN, B. N. MEKHEDOV and L. N. SUKHOTIN, *Zh. Fiz. Khim.*, 1972, **46**, (10), 2651-2652

A Pd filter has been developed to separate ^3H at concentration 10^{-12} from ^1H at 60-250 torr. Range of temperature for concentration of ^3H with low specific activity is 200-250°C; for exclusion of tritiated "memory" filters it is above 350°C.

HETEROGENEOUS CATALYSIS

Concentrated Nitric Acid Made at Lower Pressure

R. J. R. HANBURY, *Chem. Engng.*, 1972, **79**, (29), 50-51

The Peroxide process produces concentrated HNO_3 from dilute (<68%) HNO_3 , liquid N_2O_4 and air at ~8 atm. Air and NH_3 are reacted over Rh-Pt catalyst gauze to form NO , from which the dilute acid is produced.

Some Recent Developments in Nitric Acid Manufacture

Nitrogen, 1972, (79, Sept./Oct.), 23-27

Developments in catalysts and pollution control in HNO_3 production and new processes for direct concentrated HNO_3 production are described. Pt catalysts may be recovered by introducing a heat-resistant stainless steel mesh and then one or two 20% Au-Pd gauzes immediately downstream

of the catalyst gauze. Pt is captured from the gas stream by exchange with Pd and is then re-processed. Pt or Pd on honeycomb or spherical supports is used in the catalytic reduction of tail gas to control pollution.

Two Regions of Platinum Crystallisation on the Surface of Aluminium Oxide

N. M. ZAIDMAN, *Kinet. Kataliz*, 1972, **13**, (5), 1254-1257

Studies on the dispersion of Pt on Al_2O_3 reveal two regions of crystallisation differing in structure and in the stoichiometric reaction of H_2 with surface Pt atoms. In one region there is a critical size of nucleus for crystallisation and isolated Pt atoms; in the other there are trimeric crystals at relatively low temperatures in two types, the sizes of which decrease as the temperature of roasting increases.

Effect of the Metal Particle Size in Supported Catalysts on the Selectivity and the Reaction Mechanisms

C. COROLLEUR, F. G. GAULT, D. JUTTARD, G. MAIRE and J. M. MULLER, *J. Catalysis*, 1972, **27**, (3), 466-468

10% Pt/ Al_2O_3 and Pt/ SiO_2 catalysts, prepared by several methods to give different mean crystallite diameters (d), gave selectivity in methylcyclopentane hydrogenolysis dependent on particle size; isomerisation of hexane occurred by a cyclic mechanism except when $d > 150\text{\AA}$; interconversion between methylpentanes occurred by a cyclic mechanism when $d < 50\text{\AA}$ but predominantly by bond shift for $d > 50\text{\AA}$. d influences the formation of various types of defects which are responsible for the different reaction mechanisms.

Catalytic Properties of Platinum Catalysts. Relative Activity of Various Platinised Carbons in Pulsed Regime Conditions

O. V. BRAGIN, K.-KH. SHNABEL', A. V. PREOBRAZHENSKII and A. L. LIBERMAN, *Kinet. Kataliz*, 1972, **13**, (5), 1204-1208

The basis of the catalytic activity of 11% Pt/C in C_8 -dehydrocyclisation of isooctane, hydrogenolysis of cyclopentane, dehydrogenation of cyclohexane, and configurational isomerisation of *cis*-1,2-dimethylcyclopentane to the *trans* form was studied by the impulse method. More activity is possessed by catalysts impregnated and not promoted by KOH. Catalysts using C calcined at 1000°C are somewhat more active than those using C heated to 300°C.

Selective Hydrogenation Catalysed by Polymeric Palladium and Platinum Complexes

H. S. BRUNER and J. C. BAILLAR, *J. Am. Oil Chem. Soc.*, 1972, **49**, (9), 533-534

PtCl_2 and PdCl_2 complexes, with organic polymeric ligands containing diphenylbenzylphosphine groups, are highly selective in the hydro-

genation of soybean methyl ester. The products are monoenes and dienes with little increase in saturation. The catalysts are heterogeneous analogues of $\text{PtCl}_2(\text{PPh}_3)_2$ and $\text{PdCl}_2(\text{PPh}_3)_2$; they are recovered easily from the system.

Selective Hydrogenation of Naphthalene and of Alkyl-naphthalenes on Palladium Catalyst

E. YA. GAMBURG, A. B. VOL'EPSHTEIN and A. D. BERENTS, *Neftekhimiya*, 1972, 12, (5), 647-651

Naphthalene and its alkyl derivatives can be hydrogenated selectively to tetralin and alkyl-tetralins over Pd catalyst at 10-150 atm, 240-300°C practically without formation of decahydro derivatives. The yield of tetrahydro derivatives is raised by increased alkyl substitution. The effects of S content and of process parameters on the conversion are given.

Investigation of the Chemisorption of Allyl Alcohol on Palladium Catalysts

V. M. VARUSHENKO, G. A. BOGDANOVSKII, L. N. KUZ'MICHEVA and B. D. POLKOVNIKOV, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1972, (10), 2326-2328

The stage of charging of a Pd surface by unreduced chemisorbed particles can be estimated from charging curves and potential curves in the α -phase region. Adsorption of allyl alcohol on Pd is accompanied by dehydrogenation, hydrogenation and destructive decomposition. Borided Pd is more active for isomerisation and for destructive reactions than is Pd black.

Differential Determination of the Surfaces of Complex Catalysts by the Chromatographic Method. III. Palladium on Aluminium Oxide

N. E. BUYANOVA, N. B. IBRAGIMOVA, A. P. KARNAUKHOV and N. G. KOROLEVA, *Kinet. Kataliz*, 1972, 13, (5), 1295-1302

Static and chromatographic measurements of surface area and dispersion of $\text{Pd}/\text{Al}_2\text{O}_3$ for O_2 chemisorption at room temperature were in good agreement. O_2 chemisorption gives a better value for Pd dispersion than does CO chemisorption. O_2 and CO adsorption isotherms on Pd black at 25°C were measured. The specific chemisorption of these gases on Pd was explained, the adsorption isotherms of them on $\gamma\text{-Al}_2\text{O}_3$ were determined, and the correction for adsorption by the catalyst support was calculated.

Catalytic Oxidation of Carbon Monoxide on Palladium and on it Promoted with Oxides V_2O_5 and Cr_2O_3 . Conditions of Transition of the Reaction to Heterogeneous-Homogeneous Regime

N. A. BOLDYREVA, V. A. ROITER, N. A. STUKANOVSKAYA and G. V. PIPKO, *Kinet. Kataliz*, 1972, 13, (6), 1475-1481

Differential calorimetric studies in flow conditions at 1 atm showed that oxidation of CO in volume

occurs by a heterogeneous-homogeneous mechanism at 226°C on Pd/BaSO_4 promoted with Cr_2O_3 , and at 257°C on Pd/BaSO_4 promoted with V_2O_5 to give complete conversion to CO_2 . Calculations confirm that the reaction can occur over metallic Pd in these conditions. A scheme for the heterogeneous-homogeneous oxidation of CO over Pd promoted with V_2O_5 and Cr_2O_3 is proposed.

Hydrocracking of Saturated Hydrocarbons

H. PICHLER, H. SCHULZ, H. O. REITEMEYER and J. WEITKAMP, *Erdöl Kohle*, 1972, 25, (9), 494-505

Extensive experimental material is reported and interpreted concerning hydrocracking of numerous pure feed hydrocarbons using Pd/Ca-Y-zeolite and Co-Mo catalysts.

Formation of Dimethyl Ether from Hydrogen and Carbon Dioxide over a Graphite-PdCl₂-Na Catalyst

S. NAITO, O. OGAWA, M. ICHIKAWA and K. TAMARU, *J. Chem. Soc., Chem. Commun.*, 1972, (23), 1266

$\text{PdCl}_2\text{-Na}$ /graphite shows good reactivity and selectivity for the formation of dimethyl ether from H_2 and CO . O_2 inhibits the reaction but CH_3OH and HCHO enhance it. Other transition metal chlorides show poor reactivity or selectivity.

Catalytic Oxidation. V. Mechanisms of Olefin Oxidation over Supported Iridium

N. W. GANT and W. K. HALL, *J. Catalysis*, 1972, 27, (1), 70-78

The selectivity and kinetics of oxidation of 2-5C olefins over $\text{Ir}/\alpha\text{Al}_2\text{O}_3$ and Ir/SiO_2 were studied. CH_3COOH was the most important product of all but *t*-butene and isobutene. A double bond cleavage mechanism was proposed.

Kinetics of the Catalytic Vapour Phase Carbonylation of Methanol to Acetic Acid

K. K. ROBINSON, A. HERSHMAN, J. H. CRADDOCK and J. F. ROTH, *J. Catalysis*, 1972, 27, (3), 389-396

Low pressure carbonylation of MeOH to AcOH is catalysed in the vapour phase by I^- -promoted Rh/C , an analogue of the homogeneous catalyst used for the reaction in the liquid phase. In both phases the reaction is first order in I^- and independent of $[\text{MeOH}]$ and $[\text{CO}]$, suggesting similar mechanisms.

Activation of Nitrogen by Alkali Metal Promoted Transition Metal. I. Ammonia Synthesis over Ruthenium Promoted by Alkali Metal

K.-I. AIKA, H. HORI and A. OZAKI, *J. Catalysis*, 1972, 27, (3), 424-431

The rate of NH_3 synthesis over Ru is greatly increased by addition of alkali metals (effect of $\text{Cs} > \text{K} > \text{Na}$). At 250°C, the rate over K-promoted 5% Ru/C is 10 times the rate over K_2O -promoted $\text{Fe}/\text{Al}_2\text{O}_3$. It is suggested that the

alkali metal increases the electron density in Ru, thus promoting activation of N₂, and that active C and Al₂O₃, which further increase the rate when used as supports, act as a medium for the electron transfer.

Differential Determination of the Surface of Mixed Catalysts by the Chromatographic Method. IV. Ruthenium on Supports

N. E. BUYANOVA, A. P. KARNAUKHOV, N. G. KOROLEVA, I. D. RATNER and O. N. CHERYAVSKAYA, *Kinet. Kataliz*, 1972, **13**, (6), 1533-1539

Differential determination of the surface of Ru catalysts by selective chemisorption of O₂ at room temperature by static and impulse methods are in agreement. CO is a less suitable adsorbate because of a possible change in the ratio of the bridging and linear forms of chemisorption. Electron microscopy gave metal particle sizes in agreement with those from chemisorption determinations.

Catalytic Deuteration of Cyclohexanone and Allied Reactions over Platinum Metals

Y. TAKAGI, S. TERATANI and K. TANAKA, *J. Catalysis*, 1972, **27**, (1), 79-88

Over Os, Ir and Pt cyclohexanone undergoes addition with D₂ but over Ru, Rh and Pd isotopic exchange also occurs leading to polydeuterated alcohols. A cyclohexanone hydrogenation mechanism is suggested consisting of three inter-linked paths, each having a different intermediate.

Hydrogenation of Carbons Catalysed by Transition Metals

A. TOMITA and Y. TAMAI, *J. Catalysis*, 1972, **27**, (2), 293-300

Using thermogravimetric analysis and gas chromatography, some noble metals were found to have high catalytic activity for the formation of CH₄ from C under 1 atm H₂, up to 1050°C. At moderate temperatures, the order of activity is Rh > Ru > Ir > Pt > Ni > Pd > Co > Fe. CH₄ is produced in stages, the pattern of formation depending on the catalyst, the type of C and the method of metal-C mixture preparation.

HOMOGENEOUS CATALYSIS

Some Chemical Conversions and the Catalytic Activity of Platinum-Acetylene Complexes

M. G. VORONKOV, V. B. PUKHNAREVICH, S. P. SUSHCHINSKAYA, L. I. KOPYLOVA and B. A. TROFIMOV, *Zh. Obshch. Khim.*, 1972, **42**, (12), 2687-2691

4- and 6-coordination complexes of Pt chloride with *tert*-butylacetylenes were formed from H₂PtCl₆ and isopropanol. They appear to be more active for hydrosilylation than previous catalysts and the reaction mechanism also appears to be different.

Homogeneous Platinum(II)-catalysed Hydrogen-Deuterium Exchange at a Saturated Carbon Atom

C. MASTERS, *J. Chem. Soc., Chem. Commun.*, 1972, (23), 1258-1259

In the presence of K₂PtCl₄, RC(CH₃)₂CH=CH₂ alkenes (R has 1-4C) undergo H-D exchange in the alkyl chain almost exclusively at C-5. A five-membered ring intermediate is suggested.

The Activation of Saturated Hydrocarbons by Transition-metal Complexes in Solution. Part II. Hydrogen-Deuterium Exchange in Saturated and Unsaturated Hydrocarbons Catalysed by Solvated Platinum(II) Chloro-complexes. Part III. Use of Photoelectron Spectra of Halogen-substituted Hydrocarbons and Hydrocarbons Containing Quaternary Carbon Atoms to Interpret the Nature of Platinum(II)-catalysed Hydrogen-Deuterium Exchange

R. J. HODGES, D. E. WEBSTER and P. B. WELLS, *J. Chem. Soc., Dalton Trans.*, 1972, (23), 2571-2576, 2577-2583

II. The effects were investigated of concentration and solvent and catalyst compositions on H-D exchange in alkanes and aromatic hydrocarbons, catalysed by platinum(II) chloro-complexes in acetic [³H₁] acid in D₂O. Cl:Pt ratios of 4.0-2.3 were used. Exchange rate varied exponentially with ionisation potential of the hydrocarbon, except when extensive complex formation occurred. III. Halogen-substituted alkanes, aromatic compounds and certain branched-chain hydrocarbons were studied by photoelectron spectroscopy and in H-D exchange reactions catalysed by PtCl₄²⁻. The exchange rates are discussed in relation to ionisation potentials and the electrons they involve.

Reduction of Carbon Dioxide by Molecular Hydrogen in the Presence of Complexes of the Transition Metals

I. S. KOLOMNIKOV, T. S. LOBEEVA and M. E. VOL'PIN, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1972, (10), 2329-2330

Various Pt metal complexes were tested as catalysts for HCOOCH₃ synthesis from CO₂, H₂ and CH₃OH. (PPh₃)₂IrH₃ gave the highest yield of the complexes tested.

Homogeneous Hydrogenation of Unsaturated Compounds Catalysed by Pd Complexes. I. Scope and Effect of Variables. II. Deuterio-genation of Mono- and Diolefins

E. W. STERN and P. K. MAPLES, *J. Catalysis*, 1972, **27**, (1), 120-133, 134-141

I. Catalysis of the hydrogenation of unsaturated compounds by Pd complexes was studied. Conversion rate and product distribution were dependent on the catalyst and nature of the

substrate. O₂ treatment of Pd(o) complexes increased the rate. Pd hydrides are probably the active species. II. Deuteration of olefins catalysed by (Ph₂PCHPh₂)₃Pd₂ on several substrates was studied to determine the mechanism of olefin hydrogenation.

Catalysis by Metal Complexes. VII. Hydro-silation Catalysed by Tetrakis(ethylene)dichlororhodium(I)

P. SVOBODA, M. ČAPKA and J. HEIFLEJŠ, *Coll. Czech. Chem. Commun.*, 1972, **37**, (9), 3059-3062

The competitive addition of couples of silicon hydrides of the type (C₂H₅)_{3-n}SiHCl_n, where n=0-3, to 1-heptene catalysed by [RhCl(C₂H₄)₂]₂ was found to yield only the products of the addition of the hydride containing the greater number of Cl atoms, in contrast to preparative additions which give individual hydrosilation products in 40-65% yields. The reason for this discrepancy is discussed.

Polymerisation of Propadiene. III. Catalyst Systems Based on Various Rhodium(I) Complexes

J. P. SCHOLTEN and H. J. VAN DER PLOEG, *J. Polymer Sci., Pt. A-1: Polymer Chem.*, 1972, **10**, (10), 3067-3076

The catalysis of the polymerisation of propadiene to 1,2-polyallene by various Rh(I) complexes was investigated. It was found that activity decreases in the order: *cis*-Rh(CO)₂P(C₆H₅)₃Cl > [Rh(CO)₂Cl]₂ > Rh(CO)₃Cl; Rh[P(C₆H₅)₃]₂(CO)Cl and Rh[P(C₆H₅)₃]₃Cl were inactive. A mechanism is proposed in which the formation of a common intermediate from propadiene and different complexes is the rate-determining step.

Fluorophosphine Complexes of Rhodium(I). Part III. Ligand-exchange Studies in Some Dimethylaminodifluorophosphenorhodium(I) Complexes

D. A. CLEMENT and J. F. NIXON, *J. Chem. Soc., Dalton Trans.*, 1973, (2), 195-200

[RhCl(C₂H₄)₂]₂ reacts with an excess of Me₂NPF₂ at room temperature to give RhCl(PF₂NMe₂)₃; in a 1:4 ratio they give the dimeric complex [RhCl(PF₂NMe₂)₂]₂. Both complexes exist as discrete entities in solution and both catalyse the decarbonylation of benzaldehyde.

Selective Catalytic Route to Bifunctional Silanes. Catalysis by Rhodium and Ruthenium Complexes of the Alcoholysis of Diarylsilanes and the Hydrosilylation of Carbonyl Compounds

R. J. P. CORRIU and J. J. E. MOREAU, *J. Chem. Soc., Chem. Commun.*, 1973, (2), 38-39

RhCl(PPh₃)₃ and RuCl₂(PPh₃)₃ are effective catalysts for the selective production of diarylalkoxysilanes by the alcoholysis of diarylsilanes

and by the hydrosilylation of carbonyl compounds; the Rh complexes are the more efficient.

Kinetics of Ethylene Polymerisation and Butadiene Polymerisation Catalysed by Solutions of Hydrido-chloro-tris(triphenylphosphine)ruthenium(II)

B. R. JAMES and L. D. MARKHAM, *J. Catalysis*, 1972, **27**, (3), 442-451

Polymerisation of C₂H₄ and of C₄H₆, catalysed by HRuCl(PPh₃)₃ in *N,N*-dimethylacetamide at 50-85°C, is first order in catalyst and in C₂H₄ in the former system but independent of [C₄H₆] in the latter, due to stronger complexing of the diene. A common mechanism is proposed where, after coordination of the monomer to the metal, the polymer chain grows by insertion of the monomer at a polarised Ru-C bond. The catalyst can be regenerated by H₂.

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

V. Z. SHARF, L. KH. FREIDLIN, V. N. KRUTH and T. V. LYSYAK, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1972, (10), 2195-2198

KOH promotes cyclohexanone reduction via H₂ transfer from pentanol-2 with subsequent hydrogenation and condensation in the presence of RuCl₂(Ph₃P)₃. H₂ transfer is greatest for KOH concentrations 1.64 × 10⁻³M in Ar or 4.08 × 10⁻³M in H₂. As KOH concentration rises so does the hydrogenation by H₂ and the condensation. H₂ transfer increases from 50°C to 84°C, but hydrogenation is maximum at 70°C, due to the catalytic action of various intermediates.

FUEL CELLS

Low Power Methanol-Air Battery

J. PERRY, *Extended Abstr., 142nd Natl. Mtg., Electrochem. Soc.*, 1972, **72-2**, 29-31, abstr. 9

A nine-cell stack weighing 5.6 lb operated in a 600/6s, 45mW/15W duty cycle for more than 1000 h before failure due to leakage. Each cell contained a PTFE-bonded anode containing 25% Pt-Pd catalyst, two cathodes containing Ag, MeOH-KOH electrolyte and an air inlet.

Oxygen-Hydrogen Fuel Cells. VII. A Hydrogen Permeable Electrode of Palladium-Silver Alloy

T. SHIROGAMI, *Denki Kagaku*, 1972, **40**, (5), 390-395

The diffusion coefficient of H in a 25 at.% Ag-Pd electrode is half that in pure Pd, necessitating only half the thickness of metal. The alloy electrode showed no deterioration after repeated absorption and desorption of H.

Hydrogen-permeable Electrodes of Pd-Ag-Au Alloy

T. SHIROGAMI, *Denki Kagaku*, 1972, 40, (8), 605-610

The ternary alloy 66.6 wt.% Pd-13.4 wt.% Ag-20 wt.% Au combines good polarisation characteristics with excellent mechanical properties for use as a H-permeable membrane electrode with a high resistance to pinholing. The lattice parameter and electrode potential as a function of dissolved H were measured and the diffusion coefficient of H through the membrane was determined.

Preparation of Highly Dispersed Platinum on Carbon

K. F. BLURTON, *Carbon*, 1972, 10, (3), 305-315

The preparation, characterisation and properties of Pt-doped C for fuel cell electrodes are described. A high degree of dispersion of Pt (crystallites $<15\text{\AA}$) was achieved only by pyrolysis at 500-800°C of the Ca^{2+} form of Amberlite IRC50 and CG50 resins on which Pt ions had been localised by exchange. The mechanism and influence of the pyrolysis are discussed.

TEMPERATURE MEASUREMENT

Resistance Thermometry in Magnetic Fields. I. Thermistors and Platinum Thermometers at 77K

J. E. VEVAI, D. G. ELLIOT and W. I. HONEYWELL, *Cryogenics*, 1972, 12, (3), 192-195

At 77K, in magnetic fields up to 16 kG, both negative temperature coefficient thermistors and Pt resistance thermometers show a virtual rise in

temperature due to the field. Pt thermometers seem more desirable for this application.

The Calibration of Resistance Thermometers at Low Temperatures

R. L. RUSBY, M. V. CHATTLE and D. M. GILHEN, *J. Phys. E, Sci. Instrum.*, 1972, 5, (11), 1102-1105

Details are given of an apparatus for comparing resistance thermometers at 4-90K and for the routine calibration of Pt resistance thermometers in accordance with IPTS-68.

The Automatic Calibration of Platinum-Platinum, Rhodium Thermocouples in the Temperature Range 0 to 1100°C

T. P. JONES, *Aus. J. Instrum. Control*, 1972, 28, (4), 91-96

Equipment for the automatic calibration of Pt : Rh-Pt thermocouples from 0-1100°C is described. The uncertainty of calibration is only $\pm 0.3^\circ\text{C}$ and the time for calibration is 1 h compared to 46 h for the fixed-point method.

A Centralised Temperature Control System for Diffusion Furnaces

G. J. FULLIN and N. BAHNCK, *Solid State Technol.*, 1972, 15, (11), 40-43, 48

The installation of a centralised temperature control system at the Allentown Works of Western Electric Co., Inc., has led to increased yields and significant savings in the manufacture of diffused-junction npn transistors. The system uses three Pt : 10% Rh-Pt in each of 35 diffusion furnaces. Automatic, continuous temperature measurement gives close control over quality, enabling a sampling method of testing to be established.

NEW PATENTS

METALS AND ALLOYS

Tarnish Resistant Alloys

PENNWALT CORP. *British Patent* 1,296,879

An alloy which resists tarnishing contains 39-47% Au, 9-12% Pd and the balance Ag and Cu in a 1:1-1.5:1 ratio. The alloy can be used for jewellery, dental work and electrical contacts.

Dental Gold Alloy

L. HIRSCHBORN *U.S. Patent* 3,679,402

A gold alloy for bonding to dental porcelain for capping teeth contains 67.7 wt.% Au, 16.7% Pd, 11.6% Pt, 1.3% Ru, 2.0% Ag, 0.6% Sn, 0.1% Cu.

Degassed Platinum Powders

E. I. DU PONT DE NEMOURS & CO.

U.S. Patent 3,674,515

Degassed Pt powders are prepared by mixing

finely divided Pt with at least an equal volume of a diluent metal oxide powder, heating the mixture to dissipate all gases from the Pt powder, cooling the mixture and separating the Pt from the diluent. The Pt powders are suitable for application to "green" ceramic sheets used to produce monolithic multi-layer ceramic circuit components.

Platinum Group Metal Alloys

JOHNSON MATTHEY & CO. LTD.

U.S. Patent 3,676,114

Pt group metal alloys, especially 9-45 (preferably 20-40) wt.% Rh-Pt, are dispersion hardened by the presence of up to 1 wt.% of Ti, V, Zr, Nb, Hf and/or Ta.

Superconducting Alloy

M. WILHELM et al.

U.S. Patent 3,684,495

A superconducting alloy has the formula