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

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

Revised values of the enthalpies of pure Pt and 10 wt.% Rh-Pt from 400-1700°K 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

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

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

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

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 x 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

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_{liq.He}.

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

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 a-Pd are not occupied, the effective valency then being four.

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

Phase diagrams of Pd-Ln alloys were determined by D.T.A., X-ray diffraction and metallographic techniques. In general seven phases occurred: LnPd, LnPd, and LnPd (and LnPd, when Ln=Y, Dy, Er), all melting congruently; and
Ln₃Pd₄, Ln₅Pdₓ, and LnPd₄ (and Ln₃Pd₄ when Ln = Sm, Gd, Ho), formed by peritectic reactions. Structural data are given for LnPd₃, LnPd, Ln₅Pdₓ and LnPd₄.

Excess Specific Heat of a Glassy Pd₀.₇₇₅ Cu₀.₆₆₅ Si₀.₁₆₅ Alloy at Low Temperature
The specific heat of Pd₀.₇₇₅ Cu₀.₆₆₅ Si₀.₁₆₅ 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.

Electrical Resistivity of Ruthenium at High Temperatures
The electrical resistivity of Ru was measured in the range 293–2275 K and an expression was derived to T⁴. Values for the temperature coefficient of resistivity are given.

On the Constitution of the Rhodium-Lead System
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
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
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
The complete phase diagram is established for the Ru-Ti-Hf system.

CHEMICAL COMPOUNDS

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

The Electrical Conductivity Behaviour of K₃Pt(CN)₄BrO₃·2·3H₂O at High Pressures
K₃Pt(CN)₄BrO₃·2·3H₂O 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. Záš, J. Drobník and Z. Režný, Neoplasma, 1972, 19, (4), 305–310
After an intraperitoneal injection of 8 mg/kg cis-Pt(NH₃)₂Cl₂, 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 H₂ Histocompatibility
Maximum suppression of skin graft rejection in mice by cis-Pt(NH₃)₂Cl₂ 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)
The antitumour compound, cis-Pt(NH₃)₂Cl₂, was synthesised from metastable¹⁹⁵Pt; its structure was verified by chemical and biological methods. Following i.v. injection into rabbits.
there was widespread distribution then ac-
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(NH₂)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
3694-3699
The preparation and structure of the hydroxy-
bridged complexes [M₂(OH)₂L₂][BF₄]₂, where
M=Pt and L=trihexylphosphine, triphenyl-
phosphine or pyridine, or where M=Pd and
L=triphenylphosphine, are described. These com-
plexes 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 super-
conducting 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 Pal-
ladium 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 black 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 con-
tamination 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 carbolyl-chloride or
acetylacetone 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 Hydro-
phobic Surfaces
W. P. TOWNSEND, J. A. EMERSON and J. T. KENNEY,
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(I) 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. SOBEKIVICH, Zh. Prikladnoi
Khim., 1972, 45, (9), 1948-1953
Properties of Pd-Co electrodeposits depend on the
conditions of electrolysis. Dispersion of Pd-Co
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, Nitrosochloride and Sulphamine Electrolytes for Ruthenation

V. V. VYACHESLAVOV and E. P. LEONENKO, Zh. Prikladnoi Khim., 1972, 45, (8), 1728–1733

Studies of sulphate, nitrosochloride and sulphamate electrolytes prepared from Ru hydroxochloride 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 $^1$H and $^3$H on a Palladium Filter


A Pd filter has been developed to separate $^3$H at concentration $10^{-11}$ from $^1$H at 60–250 torr. Range of temperature for concentration of $^3$H with low specific activity is 200–250°C; for exclusion of tritiated “memory” filters it is above 350°C.

HETERGENEOUS CATALYSIS

Concentrated Nitric Acid Made at Lower Pressure


The Peroxide process produces concentrated HNO₃ from dilute (<68%) HNO₃, liquid N₂O₄ and air at ~8 atm. Air and NH₃ are reacted over Rh-Pt catalyst gauze to form NO, from which the dilute acid is produced.

Some Recent Developments in Nitric Acid Manufacture


Developments in catalysts and pollution control in HNO₃ production and new processes for direct concentrated HNO₃ production are described. Pt catalysts may be recovered by introducing a heat-resistant stainless steel mesh and then one or two 20% Au-Pd gauges immediately downstream of the catalyst gauze. Pt is captured from the gas stream by exchange with Pd and is then reprocessed. 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 Al₂O₃ reveal two regions of crystallisation differing in structure and in the stoichiometric reaction of H₂ 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


10% Pt/Al₂O₃ and Pt/SiO₂ 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 Å; interconversion between methylpentanes occurred by a cyclic mechanism when d < 50 Å but predominantly by bond shift for d > 50 Å. 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


The basis of the catalytic activity of 11% Pt/C in C₅-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


PtCl₄ and PdCl₂ complexes, with organic polymeric ligands containing diphenylbenzylphosphine groups, are highly selective in the hydro-

Platinum Metals Rev., 1973, 17, (2) 72
genation of soybean methyl ester. The products are monoenes and dienes with little increase in saturation. The catalysts are heterogeneous analogues of PtCl₂(PPh₃)₃ and PdCl₂(PPh₃)₂; they are recovered easily from the system.

Selective Hydrogenation of Naphthalene and of Alkynaphthalenes on Palladium Catalyst

E. YA. GAMBUK, A. B. VOL'-EPSHTIEIN and A. D. BERENTS, Neftikhimiya, 1972, 12, (5), 647-651

Naphthalene and its alkyl derivatives can be hydrogenated selectively to tetralin and alkyltetralins 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


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. Bonded 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


Static and chromatographic measurements of surface area and dispersion of Pd/Al₂O₃ for O₂ chemisorption at room temperature were in good agreement. O₂ chemisorption gives a better value for Pd dispersion than does CO chemisorption. O₂ 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 γ-Al₂O₃ 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 V₂O₅ and Cr₂O₃. Conditions of Transition of the Reaction to Heterogeneous-Homogeneous Regime


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/BaSO₄ promoted with Cr₂O₃, and at 257°C on Pd/BaSO₄ promoted with V₂O₅ to give complete conversion to CO₂. 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 V₂O₅ and Cr₂O₃ 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


PdCl₂-Na/graphite shows good reactivity and selectivity for the formation of dimethyl ether from H₂ and CO. O₂ inhibits the reaction but CH₃OH 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. CANT and W. K. HALL, J. Catalysis, 1972, 27, (1) 70-78

The selectivity and kinetics of oxidation of 2-5C olefins over Ir/αAl₂O₃ and Ir/SiO₂ were studied. CH₃COOH was the most important product of all but 1-buten and isobutene. A double bond cleavage mechanism was proposed.

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


Low pressure carbonylation of MeOH to AcOH is catalysed in the vapour phase by Ir--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 [MeOH] and [CO], suggesting similar mechanisms.

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


The rate of NH₃ synthesis over Ru is greatly increased by addition of alkali metals (effect of Cs > K > Na). At 250°C, the rate over K-promoted 5% Ru/C is 10 times the rate over K₂O-promoted Fe/Al₂O₃. It is suggested that the
alkali metal increases the electron density in Ru, thus promoting activation of N, 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


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


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 interlinked 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


4- and 6-coordination complexes of Pt chloride with tert-butylacetylenes were formed from H₂PtCl₄ 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


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


II. The effects were investigated of concentration and solvent and catalyst compositions on H-D exchange in alcanes and aromatic hydrocarbons, catalysed by platinum(II) chloro-complexes in acetic [H₄] 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 alcanes, aromatic compounds and certain branched-chain hydrocarbons were studied by photoelectron spectroscopy and in H-D exchange reactions catalysed by PtCl₄⁺. 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


Various Pt metal complexes were tested as catalysts for HCOOCH₃ synthesis from CO₂, H₂ and CH₃OH. (PPh₃)₃IrH₂ gave the highest yield of the complexes tested.

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


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(0) complexes increased the rate. Pd hydrides are probably the active species. II. Deuteration of olefins catalysed by (Ph₅PCHPPh₅)₃Pd₄ on several substrates was studied to determine the mechanism of olefin hydrogenation.

Catalysis by Metal Complexes. VII. Hydrogenation Catalysed by Tetrakis(ethylene)dichlororhodium(I)


The competitive addition of couples of silicon hydrides of the type (C₂H₅)₉nSiHCl₉, where n = 0–3, to 1-heptene catalysed by [RhCl(C₂H₅)₉]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


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)₆P(C₂H₅)₃Cl > [Rh(CO)₅Cl]Cl > [Rh(CO)₅Cl₂], Rh[P(C₂H₅)₃]₃[PF₆] and Rh[P(C₂H₅)₃]₂[PF₆]Cl were inactive. A mechanism is proposed in which the formation of a common intermediate from propadiene and different complexes is the rate-determining step.


[RhCl(C₂H₅)₃] reacts with an excess of Me₂NPF₃ at room temperature to give RhCl(PF₆)Me₂Cl; in a 1:4 ratio they give the dimeric complex [RhCl(PF₆)Me₂]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


RhCl[(PPh₃)₂] and RuCl₂(PPh₃)₂ 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 Hydridochlorotris(triphenylphosphine)rhuthenium(II)


Polymerisation of C₂H₄ and of C₅H₈, catalysed by HRuCl(PPh₃)₅ in N₂,N-dimethylacetamide at 50–85°C, is first order in catalyst and in C₂H₄ in the former system but independent of [C₅H₈] 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


KOH promotes cyclohexanone reduction via H₂ transfer from pentanol-2 with subsequent hydrogenation and condensation in the presence of RuCl₂(PPh₃)₅. H₂ transfer is greatest for KOH concentrations 1.64×10⁻⁵ M in Ar or 4.08×10⁻⁵ M 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


A nine-cell stack weighing 5.6 lb operated in a 600/68, 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.


T. SHIROMI, 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 H₂.
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 <15Å) was achieved only by pyrolysis at 500-800°C of the Ca2+ 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
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
Equipment for the automatic calibration of Pt-Rh-Pt thermocouples from 0-1100°C is described. The uncertainty of calibration is only ±0.3°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 : Rh-Pt thermocouples 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

Platinum Metals Rev., 1973, 17, (2)