

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Contribution on the Inner Oxidation of Platinum-(10% Rh)-1% Zr Alloys

G. REINACHER, *Z. Metallkunde*, 1971, **62**, (11), 835-840

The alloys 1 wt.% Zr-Pt (I) and 1 wt.% Zr-10 wt.% Rh-Pt (II) can be internally oxidised by heat treatment in air at 850 and 1000°C. At 1400°C both alloys form oxides only in the grain boundaries, which stops further oxidation. The alloys suffer a decrease in hardness with increased heat treatment temperature, the reduction being 50% with I and 10% in II.

Interdiffusion and Compound Formation in Thin Films of Pd or Pt on Si Single Crystals

J. DROBEK, R. C. SUN and T. C. TISONE, *Phys. Status Solidi, A*, 1971, **8**, (1), 243-248

Electron transmission observations of Pt-Si diffusion couples show that the compounds Pt₃Si, Pt₂Si and PtSi form during diffusion. Pt₃Si disappears as diffusion proceeds, leaving a film of a mixture of 35-40% Pt₂Si and remainder PtSi. In PdSi diffusion couples the dominant phase is Pd₂Si, with only small amounts of PdSi formed after vacuum annealing.

On the Age-hardening of Fe-Pt-Mn Alloys

M. TANAKA and T. SUZUKI, *J. Japan Inst. Metals*, 1971, **35**, (10), 974-979

Strain-hardening due to formation of a coherent zone, probably Pt-Mn β phase, is a major factor of age-hardening. There is an extended miscibility gap island compared with Fe-Ni-Mn. The strain hardening response increases in Fe-Pt-Mn alloys when precipitation of the coherent zone occurs. The f.c.t. Pt-Mn β_1 phase with Cu-Au type structure is observed in aged Fe-Pt-Mn alloys.

Electrical Resistivity and Magnetic Susceptibility of Amorphous Cr-Ni-Pt-P Alloys

A. K. SINHA, *J. Appl. Phys.*, 1971, **42**, (12), 5184-5186

Amorphous alloys of the composition (Cr_xNi_{0.30-x}Pt_{0.70})_{0.75}P_{0.25}, where $0 \leq x \leq 0.06$, were synthesised by rapid quenching of the melt. The base alloy, for which $x=0$, is non-magnetic and has a negative temperature dependence of resistivity at $4.2 \leq T \leq 400$ K. Cr additions give rise to an additional temperature dependent negative resistivity contribution. This can be correlated with the presence of localised magnetic moments on Cr atoms, and consequent Curie-Weiss behaviour of the $1/\chi$ against T curves.

Thermodynamic Properties of the Gold-Palladium System Measured with a Dual-chamber Knudsen Cell Mass Spectrometer Combination Technique

D. C. BARTOSIK, *Diss. Abstr. B*, 1971, **32**, (6), 3478B

The activity and potential heats of mixing of the components in the solid Au-Pd system at 1473K were measured. The activities of both exhibit negative deviations from ideality for alloys with >20 at.% Pd or with >80 at.% Au. The integral excess entropy and enthalpy are both negative for all alloys up to 80 at.% Au. The electronic structure of the alloys is discussed.

Imperfect Misfit Dislocations in Thin Films of Silver on Palladium

J. W. MATTHEWS, *J. Appl. Phys.*, 1971, **42**, (13), 5640-5643

A study of the energy of complete and potential misfit dislocations indicates that the misfit between a (001) Ag film and a Pd substrate will be accommodated by partial misfit dislocations. The extrinsic stacking faults associated with these partials are expected to lie in the Ag film and to modify its crystal structure.

X-ray Determinations of the Debye Temperatures and Thermal Expansions for the Pd-Ag-Au System

S. V. N. NAIDU and C. R. HOUSKA, *J. Appl. Phys.*, 1971, **42**, (12), 4971-4975

X-ray measurements of the Debye characteristic temperatures θ_m and the coefficient of thermal expansion for the Pd-Ag-Au system are presented. Lattice parameters and integrated intensities of Bragg reflections are calculated for the temperature range 80-298K. For all alloys the predominant lattice disturbance is due to thermal vibration. Grüneisen's relationship between the mean square atomic vibration amplitude and the thermal expansion for cubic solids is valid for these alloys with $\gamma Z^2 = 0.167$.

The Field Dependence of Electron-Paramagnon Scattering in Nearly Ferromagnetic Pd-Ni Alloys

A. I. SCHINDLER and B. C. LAROY, *Solid State Commun.*, 1971, **9**, (21), 1817-1820

The temperature dependence of the electrical resistivity of dilute paramagnetic Pd-Ni alloys was measured in applied magnetic fields of up to 93 kG. Increasing field strength causes the s electron-paramagnon scattering coefficient to decrease, this tendency being stronger with increasing Ni concentrations.

The Structure of the Ternary Copper-Nickel-Palladium Alloys at Temperatures from 400 to 700°C

E. RAUB, O. LOEBICH, W. PLATE and H. KRILL, *Z. Metallkunde*, 1971, **62**, (11), 826-830

The structure of ternary Cu-Ni-Pd alloys with up to 60 at.% Pd was investigated using X-rays at 400-700°C. At low Pd concentration a miscibility gap exists in which two disordered f.c.c. phases are in equilibrium below 675°C. The $\alpha_1+\beta$ two phase region exists in a wide range of ternary alloys. It is in equilibrium with the two phase region $\alpha_1+\alpha_2$ below 500°C.

Levitation Calorimetry. IV. The Thermodynamic Properties of Liquid Cobalt and Palladium

J. A. TREVERTON and J. L. MARGRAVE, *J. Phys. Chem.*, 1971, **75**, (24), 3737-3740

Levitation calorimetry was used to study the thermodynamic properties of liquid Pd. $\Delta H_m = 3940 \pm 70$ cal/g.atom, $\Delta S_m = 2.16 \pm 0.04$ cal/degK/g.atom, $C_p(l) = 9.18$ cal/degK/g.atom. The emissivity of the liquid metal surface $= 0.374 \pm 0.004$.

Large Magnetic Scattering in Fe-doped Pd-based Alloys

R. P. GUERTIN, I. TURNER and W. S. WEINTRAUB, *Phys. Lett. A*, 1971, **37A**, (4), 309-310

The low-temperature electrical resistivity of several paramagnetic Pd-based alloys with ~ 1000 p.p.m. Fe was measured. A very large contribution to the resistivity by the Fe impurity is observed for both the Pd-Rh and Pd-Pt series.

Magnetic States in Amorphous Fe-Pd-Si Alloys

R. HASEGAWA, *J. Phys. Chem. Solids*, 1971, **32**, (11), 2487-2492

The electrical resistivity, magnetic susceptibility and magnetoresistivity of amorphous $Fe_x(Pd_{82}Si_{18})_{100-x}$, where x varies between 0.1 and 0.9, were measured. The polarisation of the d-electrons of Pd atoms around a Fe atom persists down to the lowest Fe concentration. No giant moment is observed. Interactions between the d-electrons of the Fe atoms, resulting in a supermagnetic behaviour of the alloys below a characteristic temperature, occurs only at higher fields.

Mössbauer Effect Study of Amorphous Fe-Pd-Si Alloys

T. E. SHARON and C. C. TSUEI, *Solid State Commun.*, 1971, **9**, (22), 1923-1927

The Mössbauer spectra of amorphous $Fe_xPd_{80-x}Si_{20}$ (where $0 < x < 7$), were measured at 4.2, 77 and 295K. Results are not typical of a superparamagnetic system and a model is proposed for the magnetism in these alloys based on a local ferromagnetic order whose direction changes randomly throughout the material.

The Palladium-Tungsten Phase Diagram below 1100°C

H. R. KHAN and C. J. RAUB, *J. Less-common Metals*, 1971, **25**, (4), 441-442

The phase diagram for 5-90 at.% W-Pd below 1100°C was investigated. Reduction at 500-700°C gave a homogeneous phase only with 5 at.% W, samples containing more W consisting of f.c.c. Pd and b.c.c. W phases. After annealing at 700°C for 1000 h, alloys containing up to 15% at. W consisted of the f.c.c. Pd phase only. For 20-70 at.% W the f.c.c. Pd and b.c.c. W phases were present. From graphical data it is concluded that the phase boundary of the f.c.c. Pd solid solution exists between 15 and 20 at.% W at 700°C. Additional X-ray lines were observed which may be due to an intermediate phase.

Influence of the Crystalline Electric Field on the Kondo Resistivity of $Ce_xLa_{1-x}Pd_3$ Ternaries

V. U. S. RAO, R. D. HUTCHENS and J. E. GREEDAN, *J. Phys. Chem. Solids*, 1971, **32**, (12), 2755-2759

The electrical resistivities of the cubic $Ce_xLa_{1-x}Pd_3$ ternary alloys were measured at 2-300K; the alloys are all of single phase except between $0.3 < x < 0.5$. Resistivities indicate the presence of the Kondo effect, and some alloys display a maximum in their resistivity/temperature curve and also an additional minimum at low temperatures. An explanation is given in terms of the influence of the cubic crystalline field on the Ce ions.

Thermoelectric Power of Pure Rhodium

D. J. HUNTLEY, *Can. J. Phys.*, 1971, **49**, (20), 2610-2612

The thermoelectric power of Rh was measured at 4-300K. A peak of $+2\mu V/K$ was found at 145K, but none at 25K, in contrast to previous results. The reasons for the peak are discussed.

Low-temperature Heat Capacity of $Ni_{0.62}Rh_{0.38}$

B. B. TRIPLETT and N. E. PHILLIPS, *Phys. Lett. A*, 1971, **37A**, (5), 443-444

The magnetic field dependence of the anomalous heat capacity of $Ni_{0.62}Rh_{0.38}$ at low temperatures is consistent with superparamagnetic behaviour of ferromagnetic clusters, but not with spin fluctuation effects.

Metastable F.C.C. Fe-Rh Alloys and the Fe-Rh Phase Diagram

C. C. CHAO, P. DUWEZ and C. C. TSUEI, *J. Appl. Phys.*, 1971, **42**, (11), 4282-4284

Single phase metastable f.c.c. Fe-Rh alloys were prepared by rapid quenching from liquid, and the lattice spacings and Fe^{57} Mössbauer spectra were measured at room temperature, lattice parameters and isomer shifts both vary smoothly with Rh concentration.

The Ru-Sc Constitution Diagram

E. M. SAVITSKII, V. P. POLYAKOVA and N. B. GORINA, *Izv. Akad. Nauk S. S. R., Metall.*, 1971, (6), 161-163

The Ru-Sc system contains the phases Ru_2Sc , $RuSc$ and $RuSc_3$, the latter detected for the first time. Properties vary with alloy composition according to Kurnakov's Law.

CHEMICAL COMPOUNDS

On the Composition and Structure of Pt_3O_4
A. M. SUKHOTIN, E. A. GANKIN, YU. D. KONDRASHOV, YU. A. OMEL'CHENKO and B. YA. SHAL'MAN, *Zh. Neorg. Khim.*, 1971, 16, (12), 3190-3194

$PtO_{1.18}$ is prepared by thermal decomposition of hydrated PtO_2 with subsequent chemical treatment. X-ray studies showed that the synthesised oxide agreed structurally with f.c.c. Pt_3O_4 .

Tetracarbonyls of Palladium and Platinum in Low Temperature Matrices

H. HUBER, P. KUNDIG, M. MOSKOVITS and G. A. OZIN, *Nature Phys. Sci.*, 1972, 235, (57, Jan. 31), 98-100

Matrix isolation was used to stabilise simple carbonyl species of Pd and Pt for I.R. spectroscopic analysis. The species were produced by reaction of the monoatomic metal vapour and CO in Ar. Spectroscopic results indicate the presence of $Pd(CO)_4$ and $Pt(CO)_4$.

Platinum. A Noble Metal, "Base" Atoms

P. S. SKELL and J. J. HAVEL, *J. Am. Chem. Soc.*, 1971, 93, (24), 6687-6688

Pt atoms generated in vacuo from a W filament at 1950°C were deposited simultaneously with a large excess of an organic compound on the walls of the container vessel which were cooled to -196°C. The Pt atoms reacted with C_6H_6 , $1-C_4H_8$, 1,5-cyclo-octadiene and 1,3-butadiene to form organometallic complexes, some of which are catalysts.

Investigation of the Conditions of Formation of Palladium Borides

G. V. SAMSONOV, V. A. KOSENKO and V. G. IVANCHENKO, *Zh. Prikladnoi Khim.*, 1971, 44, (10), 2304-2306

Thermal, X-ray and metallographic studies analysed the direct synthesis of Pd_3B from its elements at 700-900°C for 5-6 h and of Pd_5B_2 at 800-950°C for 60-70 h. These phases melt at 1110 ± 20 and 1190 ± 20 °C respectively. The microhardness of Pd_3B is 470 ± 40 kg/mm².

Dissociation of Tris(triphenylphosphine)-chlororhodium(I) in Solution

H. ARAI and J. HALPERN, *J. Chem. Soc., D, Chem. Commun.*, 1971, (23), 1571-1572

The equilibrium constant for the dissociation of

$RhCl(PPh_3)_3$ to $RhCl(PPh_3)_2$ and PPh_3 was found spectrophotometrically to be $(1.4 \pm 0.4) \times 10^{-4}M$ in C_6H_6 at 25°C.

$La_xSr_{1-x}RuO_3$: A New Perovskite Series

R. J. BOUCHARD and J. F. WEIHER, *J. Solid State Chem.*, 1972, 4, (1), 80-86

$LaRuO_3$ was prepared for the first time; it is metallic and antiferromagnetic. Solid solutions with ferromagnetic $SrRuO_3$ of the type $La_xSr_{1-x}RuO_3$ exist for all values of x; ferromagnetism diminishes rapidly with increasing La content. All compounds show Curie-Weiss behaviour at low temperatures. The properties and structure of $LaRuO_3$ are discussed.

Kinetics of Nitrogen Uptake by Ruthenium (II) Aqspecies

L. A. P. KANE-MAGUIRE, *J. Inorg. Nucl. Chem.*, 1971, 33, (11), 3964-3966

The kinetics of complex formation between N_2 and the Ru(II) complexes $cis-[Ru(A-A)_2(H_2O)_2]^{2+}$ ($A-A = (NH_2)_4$, ethylenediamine, $\frac{1}{2}$ triethylenetetramine) were studied. The species $[Ru(A-A)_2(H_2O)N_2]^{2+}$ and $([Ru(A-A)_2(H_2O)]_2N_2)^{4+}$ were identified by U.V. spectrometry. The kinetic results show the formation of the N_2 complexes to be almost independent of the Ru complex used.

Oxidative Addition Reactions of Triphenylphosphine with Dodecacarbonyltriosmium(O): Benzyne-, Phenyl-, and Related Complexes of Osmium

C. W. BRADFORD, R. S. NYHOLM, G. J. GAINSFORD, J. M. GUSS, P. R. IRELAND and R. MASON, *J. Chem. Soc., Chem. Commun.*, 1972, (2), 87-89

Reaction of $Os_3(CO)_{12}$ with PPh_3 in the mole ratio of 1:2 gives a mixture of products, three of which were defined by X-ray crystallography as $HOs_3(CO)_9(PPh_3)(PPh_2C_6H_4)$, $Os_3(CO)_9(PPh_2)(Ph)(PPh_2C_6H_4)$ and $Os_3(CO)_7(PPh_2)_2(C_6H_4)$.

Beryllides of Ruthenium, Osmium, Rhodium, and Iridium of Composition M_2Be_{17}

L. F. VERKHOROBIN, G. P. KOVTUN, A. A. KRUGLIKH, N. N. MATYUSHENKO, N. S. PUGACHEV and G. F. TIKHINSKII, *Izv. Akad. Nauk S.S.S.R., Metall.*, 1971, (6), 168-171

7-16 at.% M-Be alloys (M=Ru, Os, Rh, Ir) contain isomorphous M_2Be_{17} , structure $P6/mmm$. Lattice parameters are Ru_2Be_{17} , $a = 4.203 \pm 0.004$ and $c = 10.90 \pm 0.01$ Å; Os_2Be_{17} , $a = 4.221 \pm 0.004$ and $c = 10.95 \pm 0.01$ Å; Rh_2Be_{17} , $a = 4.190 \pm 0.004$ and $c = 10.88 \pm 0.01$ Å; Ir_2Be_{17} , $a = 4.193 \pm 0.004$ and $c = 10.89 \pm 0.01$ Å.

Synthesis, Structure and Reactions of Chelate Metal-olefin Complexes

R. S. NYHOLM, *Pure Appl. Chem.*, 1971, 27, (1-2), 127-144

Organometallic complexes in which the metal is

coordinated to an olefinic bond in the ligand are reviewed. The bonding structure, coordination, reactions and isomerisation of such compounds, many of which include Pt metals and Au, are discussed.

The Development of Transition Metal Chemistry in the United States of America

J. C. BAILAR, *Ibid.*, 1-21

The study of complex inorganic compounds in the U.S.A. over the past century is reviewed. Some Pt metal organometallic complexes are discussed as examples of specific types of complex.

ELECTROCHEMISTRY

Surface Films on Platinum and Tungsten Carbide Anodes

K. VON BENDA, H. BINDER, A. KOHLING and G. SANDSTEDE, *Battelle Frankfurt Inform.*, 1971, (11), 46-52

The electro-oxidation of CH_3OH , HCOOH , CO and H_2 on Pt anodes with adsorbed surface films was studied. The variations in oxidation rates at different potentials due to the nature of the adsorbed surface films are discussed.

The Hydrogen/Oxygen Titration of Platinum Films

M. AKHTAR and F. C. TOMKINS, *Trans. Faraday Soc.*, 1971, 67, (8), 2454-2460

The surface area of evaporated Pt films was obtained by measuring uptake of H_2 subsequent to chemisorption of O_2 at 196 K. The effect of raising the temperature in vacuo and in the presence of O_2 was studied. The surface area obtained refers to the area catalytically active for the $\text{H}_2 + \text{O}_2$ reaction at that temperature. "Active" area determinations have an accuracy of 3-4%.

Effect of Presorption on Platinum Films of Catalytic Oxidation of Hydrogen and Area Determination by Carbon Monoxide/Oxygen Titration

Ibid., 2461-2468

The effect of presorbed H_2O , CH_3OH and NH_3 on Pt films on the catalytic oxidation of H_2 at 195 K was studied. Substantial amounts of H_2 molecules were associatively chemisorbed on the presorbed primary layer of water and were rapidly oxidised by $\text{O}_2(\text{g})$. A mechanism for this process is proposed.

Role of Structural Factors in Electrocatalysis. I. Smooth Platinum Electrodes

V. S. BAGOTSKII, YU. B. VASILIEV and I. I. PYNSHNOGRAEVA, *Electrochim. Acta*, 1971, 16, (12), 2141-2167

Adsorption of H , O , CH_3OH , Br^- and HSO_4^- , evolution of H_2 and O_2 and electro-oxidation of CH_3OH were studied on different faces of a Pt monocrystal and on annealed polycrystal samples

with structural defects. Adsorption isotherms were almost identical, but process rates on faces with densest atomic packing were highest. Neither unsaturated surface atoms nor lattice defects act as active centres governing the catalytic properties of the whole surface. The bond energy changes little from one face to another of the monocrystal or with the number of defects. The shape of the adsorption isotherm seems to be governed by electronic properties.

Study of the Kinetics of Electrochemical Reactions by Thin Layer Voltammetry. IV. Influence of Chemisorbed Species on the Reactions of Platinum Complexes at Platinum Electrodes

A. L. Y. LAU and A. T. HUBBARD, *J. Electroanal. Chem. Interfac. Electrochem.*, 1971, 33, (1), 77-93

The rates of electrode reactions of acidoammine Pt (II) and (IV) complexes were measured in halide solutions using Pt electrodes treated with irreversibly chemisorbed substances. The chemisorbed substances displaced most of the specifically adsorbed halide, shifted the potentials in the diffuse double layer to more positive values and sterically hindered the reactions.

Proton Injection in the Highly Conducting Mixed Valence Square Planar Platinum Complex $\text{K}_{1.64}\text{Pt}(\text{C}_2\text{O}_4)_2 \cdot x\text{H}_2\text{O}$. New Solid State Proton Galvanic Cell

F. N. LECRONE and J. H. PERLSTEIN, *J. Chem. Soc., Chem. Commun.*, 1972, (2), 75-74

Single crystals of $\text{K}_{1.64}\text{Pt}(\text{C}_2\text{O}_4)_2 \cdot x\text{H}_2\text{O}$ display non-ohmic behaviour in applied electric fields which is associated with proton injection at the anode. The half cell reactions associated with this proton migration constitute a new solid state proton battery with cell potential in the range 0.3-0.5 V.

Hydrogenation of Propargyl Alcohol at Controlled Potentials on Palladium

N. A. ZAKARINA, G. D. ZAKUMBAEVA and D. V. SOKOL'SKII, *Zh. Fiz. Khim.*, 1971, 45, (12), 3097-3101

The rate and selectivity of hydrogenation of propargyl alcohol on Pd can be controlled by imposing a potential on the catalyst. The absolute selectivity of saturation of propargyl alcohol in allyl alcohol is reached at positive potentials.

ELECTRODEPOSITION AND SURFACE COATINGS

A Technique for Selective Electroless Plating

N. FELDSTEIN and T. S. LANCSEK, *R.C.A. Rev.*, 1971, 32, (2), 306-310

A process for the selective electroless plating of metals on dielectric substrates involves the selective deactivation of an adsorbed stannous layer

above specially patterned films. The principal reactions are discussed. The process results in the formation on the substrate surface of finely divided catalytic Pd nuclei which are essential for the initiation of the plating process.

Universal Electroplating Instrument for Gold, Rhodium, Platinum Baths, etc.

Pinturas y Acabados Ind. (Barcelona), 1971, 13, (59), 100-104

A universal laboratory plating unit suitable for the electrodeposition of Au and Pt group metals is described.

HETEROGENEOUS CATALYSIS

Sumitomo CNA/WNA Process. Integrated High Pressure Nitric Acid Plant

Nitrogen, 1971, (74), 38-39

Sumitomo Chemical Engineering Co. have developed a system capable of producing 98 wt.% and 70 wt.% HNO₃ in any desired proportion. NH₃ is burnt with air over a Pt-Rh gauze catalyst, giving an NO yield of 96%. The concentrated acid is obtained by adsorption of further N oxides in moderate strength acid followed by distillation.

Dual Catalysis Increases the Efficiency of Ammonia Oxidation

Nitrogen, 1971, (74), 41

A procedure developed by the Polish Instytut Nawozow Sztucznych combines the use of a Pt or Pt-Rh gauze and a fixed bed metal oxide catalyst such as a mixture of Cr₂O₃, Fe₂O₃, graphite and an oxide promotor. This gives substantial reduction in the excess O₂ required for a given conversion efficiency; NO₂ formation is kept to a minimum and the resultant condensate is of very low strength.

Effect of Electrolyte Composition on Charging Curves of Skeleton Platinum-Iridium Catalysts

A. D. SEMENOVA, N. V. KROPOTOVA and G. D. VOVCHEKNO, *Vest. Moskov. Univ., Ser. II, Khim.*, 1971, (5), 619-620

Electrolyte composition affects the amount of H₂ adsorbed by Pt-Ir catalysts and the adsorption energy. Adsorption capacity decreases in the order HCl, H₂SO₄, KOH.

Effect of Thermal Treatment on the Properties of Platinum Catalysts

L. I. STOLYARENKO and A. V. VASEV, *Elektrokhimiya*, 1971, 7, (9), 1380-1382

The amount of O₂ absorbed during heat treatment was measured for three Pt black catalysts prepared by different methods. The increased stability of one catalyst was due to the preparation process in which intense reaction of Pt and O₂ took place. Increase in the surface O₂ concentration increases the stability for heat treatment.

Hydrogenation of 3,7-Dimethylenebicyclo-[3,3,1]-nonane on Platinum Catalysts

F. N. STEPANOV, E. N. MARTYNOVA, L. A. ZOSIM, A. G. YURCHENKO and A. P. KRASNOSHCHER, *Zh. Org. Khim.*, 1971, 7, (12), 2516-2519

In addition to the three stereoisomeric 3,7-dimethylenebicyclo-[3,3,1]-nonanes formed during the hydrogenation of 3,7-dimethylenebicyclo-[3,3,1]-nonane over Pt in various solvents there are products of incomplete hydrogenation.

The Preparation of Pt-Alumina Catalyst and Its Role in Cyclohexane Dehydrogenation

R. W. MAATMAN, P. MAHAFFY, P. HOEKSTRA and C. ADDINK, *J. Catalysis*, 1971, 23, (1), 105-117

The preparation from H₂PtCl₆ and properties of Pt/Al₂O₃ were studied. Catalytic activity for dehydrogenation of cyclohexane at 150°C depended on Pt concentration, not on the preparation method. Dehydrogenation is zero order at atmospheric pressure and 150°C.

Catalytic Reforming of Petroleum on Platinum/Alumina Catalysts Promoted by Rare Earth Elements

N. S. KOZLOV, V. A. POLIKARPOV, G. M. SEN'KOV and V. V. SHIPIKIN, *Khim. Tekhnol., Topliv. Masel*, 1972, (1), 1-4

Tests on 0.5 wt.% Pt/Al₂O₃ with 0.1 wt.% Y and 0.05 wt.% Ce additions showed that catalysts promoted by these elements possessed greater activity, selectivity and thermal stability in petroleum reforming than unpromoted catalysts.

Effect of the Pretreatment of a Platinum/Alumina Catalyst Promoted by Yttrium on Its Activity in the Hydrogenation of Benzene

V. A. POLIKARPOV and G. M. SEN'KO, *Dokl. Akad. Nauk Belorus. S.S.R.*, 1971, 15, (6), 523-524

The activity of a Pt/Al₂O₃ catalyst was increased when promoted by 1 wt.% Y. The catalyst was preferably pretreated with H₂ at 300-400°C.

Catalytic Activity of Platinum on Delta-alumina in the Hydrogenation of Ethylene.

I. Catalytic Activity of Non-calcined Catalyst
G. PAJONK and S. J. TEICHNER, *Bull. Soc. Chim. Fr.*, 1971, (11), 3847-3855

Pt/Al₂O₃ catalyst was prepared by impregnating δ-Al₂O₃ with H₂PtCl₆ in CH₃OH. The Pt crystallite size was measured. The kinetics of hydrogenation of C₂H₄ at 0°C over this catalyst followed the Langmuir-Hinshelwood model. C₂H₄ is adsorbed associatively and inhibits the reaction; H is weakly adsorbed. The support does not affect the catalytic activity.

II. Catalytic Activity of Granulated Calcined Catalyst

Ibid., (12), 4235-4242

The activity of the calcined catalyst was 100

times less than that of the non-calcined catalyst. C_2H_4 hydrogenation follows the same mechanism. C_2H_4 is chemically and physically adsorbed on to the catalyst surface. Several explanations are advanced to account for the lower catalytic activity.

III. Catalytic Activity of the Calcined Catalyst in Powder Form

Ibid., 4242-4246

When the Pt/Al_2O_3 catalyst used above was ground into powder form the activation energy for C_2H_4 hydrogenation was lowered; the order of the reaction was unchanged. The catalytic activity/ m^2 of Pt was simultaneously increased. The activity of the catalyst is determined by its chemical not its diffusional character.

Catalytic Dehydrocyclisation of Hydrocarbons. III. Aromatisation of Hydrocarbons with Six Carbon Atoms on Chromium Oxide and Alumina or Platinum and Alumina

M. PERRÉE-FAUVET, D. HÉRAULT and B. BUIOURI, *Bull. Soc. Chim. Fr.*, 1971, (12), 4463-4470

The aromatisation of hexane, 1-hexene, 2-hexene, 2-methylpentane and methylcyclopentane was studied. Highest yields of aromatic products were obtained using Pt/Al_2O_3 ; this catalyst, however, promotes isomerisation of normal hydrocarbons into branched or cyclopentanic hydrocarbons.

Catalytic Activation of Platinum Deposited on Metallic Aluminium

S. WITEKOWA and P. MATYJEWski, *Roczniki Chem.*, 1971, 43, (10), 1729-1737

Pt/Al catalyst was prepared by precipitating Pt from H_2PtCl_6 on to Al dust. Activities of Pt/Al , Pt black and Pt /neutral carrier for oxidation were compared. The specific activity of Pt/Al was intermediate between Pt black and Pt /neutral carrier. The Pt is dispersed on the Al surface mostly in the form of a monoatomic layer.

Hydrogen Chemisorption on Platinum Catalysts

C. E. HUNT, *J. Catalysis*, 1971, 23, (1), 93-96

H_2 chemisorption on Pt and Pd on active C and Al_2O_3 was measured by rapid desorption effected by increasing the temperature from 21 to 370°C. The results show that dispersion of Pt on active C was 47, 32 and 23% for 0.5, 1.0 and 10% Pt/C .

Rapid Measurement of Hydrogen Chemisorption by Supported Catalytic Metals

H. A. BENESI, L. T. ATKINS and R. B. MOSELY, *J. Catalysis*, 1971, 23, (2), 211-213

Surface areas of catalytic metals such as $Pt/silica$ gel can be found by measuring the evolution of chemisorbed H_2 in a flowing 1 mole % H_2 -Ar mixture. The catalyst is equilibrated at 0°C and then heated to 500°C to desorb H_2 . Chemisorption values obtained for the metal surface area agree with those obtained using static techniques.

Catalytic Hydrogenation of But-2-yne on Palladium-Gold Alloys

H. G. RUSHFORD and D. A. WHAN, *Trans. Faraday Soc.*, 1971, 67, (12), 3577-3584

The hydrogenation of but-2-yne was investigated on Pd-Au wires at 263-638K. Pd-rich wires were active at the lower temperatures and Au-rich wires at the higher. Results suggest that Au acts as a diluent, the active sites being islands of four adjacent Pd atoms. The *cis/trans* ratio of but-2-enes produced fell from 99 : 1 for pure Pd to 4.2 : 1 for 97 at.% Au-Pd.

Kinetics of Selective Hydrogenation of Dimethylethynylcarbinol on Palladium in the Vapour Phase

D. Z. LEVIN, M. A. BESPROZVANNYI, F. A. MELAMED and S. L. KIPERMAN, *Kinet. Kataliz*, 1971, 12, (6), 1455-1463

Studies of the kinetics of selective hydrogenation of dimethylethynylcarbinol into dimethylvinylcarbinol in the vapour phase over Pd in a circulating system showed that the ration of the rate of reaction to the degree of conversion passes through a maximum not connected with diffusion or change of selectivity. Kinetic equations define the mechanism of the process.

Dispersion and Activity of Palladium on Aluminium Oxide

N. T. KULISHKIN, A. V. MASHKINA, N. E. BUYANOVA, A. P. KARNAUKHOV, I. D. RATNER and L. M. PLYASOVA, *Ibid.*, 1539-1545

Various methods showed that the dispersion of Pd on Al_2O_3 decreases as its concentration increases from 0.3 to 18 wt.%. The decrease is not abrupt; the total Pd surface and the activity of unit weight of catalyst increase. The specific activity for unit surface of Pd in the hydrogenation of unsaturated sulphones is not related to the dispersion of Pd.

Hydrogenation Refining of Ethylene Fraction on a Palladium Catalyst

M. SYKORA, *Chem. Prumysl*, 1971, 21, (11), 546-550

Pd catalysts for the hydrogenation of C_2H_2 to C_2H_4 were studied. With Pd/kieselguhr at constant 0.1 wt.% Pd content the activity depended on the specific carrier surface area and increased linearly with increasing surface area. The activity also increased with increased Pd content. $Pd/\alpha-Al_2O_3$ catalysts containing 0.1 wt.% Pd showed higher activity than those on kieselguhr and the activity did not depend on the specific Al_2O_3 surface area.

Properties of Palladium/Polyvinyl Alcohol Catalysts, Prepared with Alkali Additions

L. A. CHIMAROVA and O. A. TYURENKOVA, *Zh. Fiz. Khim.*, 1971, 45, (12), 3102-3105

Studies of the effect of added alkali on the activity of Pd/polyvinyl alcohol catalysts showed that

catalysts with small amounts of added alkali gave higher rates of hydrogenation of dimethylethynyl-carbinol than catalysts without alkali. As the amount added rose the rate of reduction decreased. The catalyst with alkali was adequately stable for eight months and had high selectivity.

Dealkylation of Alkylbenzenes on Rhodium/Alumina Catalyst

G. L. RABINOVICH, G. N. MASLYANSKII and L. M. TREIGER, *Kinet. Kataliz*, 1971, 12, (6), 1567-1569
Studies of the dealkylation of toluene into C_6H_6 over 0.6% Rh/ γ - Al_2O_3 at 430°C and at atmospheric pressure showed that the rate of hydrodealkylation of toluene is 2.5-2.7 times greater than that of dealkylation with H_2O vapour. Dealkylation of *m*-xylene with H_2O vapour is selective and gives toluene and C_6H_6 as products.

HOMOGENEOUS CATALYSIS

Role of Hydrogen Chloride and Characteristics of Catalyst Surface in the Oxycyanation of Ethylene

H. NAKAJIMA, *Kogyo Kagaku Zasshi*, 1971, 74, (8), 1539-1543

The synthesis of acrylonitrile from C_2H_4 , HCN and O_2 was studied over a Pd catalyst. The catalyst surface strongly adsorbs cyano ions and radicals. The rate of oxycyanation is slow but the reaction is highly selective.

Selectivity of Isomers in the Oxycyanation of Propylene over Palladium Catalysts

Ibid., 1544-1549

The oxycyanation of C_3H_6 over Pd and $PdCl_2$ was studied to measure the distribution of isomers, viz. methacrylonitrile, crotonitrile and allylnitrile. The ratios were 5 : 40 : 55 respectively with a fresh Pd catalyst, 34 : 50 : 16 with a steady state Pd catalyst and 20 : 42 : 37 over $PdCl_2$.

The Effects of the Ligands on the Oxycyanation Catalysts

Ibid., 1549-1551

Effects of ligands on the Pd catalyst in the oxycyanation of C_3H_6 were investigated. Ligands of low rank in the spectrochemical series gave high catalyst activity probably due to their decreasing the coordination strength of the cyano ion to Pd. Ligands containing I, such as iodide, iodate, periodate and *o*-iodobenzoic acid, gave the same increase in activity, due to co-ordination between the I atom and Pd atom.

A Study of the Inclusion of Dienes through π -Allyl Bonds of π -Alkenylmetalhalides. II. The Inclusion of Butadiene

L. YA. AL'T, A. I. LAZUTKINA, A. M. LAZUTKIN and YU. I. ERMAKOV, *Kinet. Kataliz*, 1971, 12, (6), 1410-1416

With π -allylpalladiumchloride and -bromide the inclusion of the first molecule of butadiene at the

π -allyl bond occurs at a rate about two orders greater than that of subsequent development of polymer chain. When π -allylpalladiumiodide reacts with butadiene, π -crotylpalladiumiodide is formed as well as polymerisation products. The reaction rate when using the chloride or bromide is in the ratio 1 : 2 to the initial catalyst concentration, and is directly proportional to the butadiene concentration.

Investigation of the Isomerisation and Hydrogenation of Olefins in the Presence of Homogeneous Palladium Catalysts on a Dimethylsulphoxide Base

L. KH. FREIDLIN, N. M. NAZAROVA and YU. A. KOPYTTSEV, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1972, (1), 201-203

The homogeneous catalyst of Pd with dimethylsulphoxide accelerates conversion of pentenes at 20°C, $p_{H_2} \approx 1$ atm. C=C bond migration in pentene-1 occurs at a greater rate than hydrogenation, and *cis*-pentene-2 is converted faster to *trans*-pentene-2 than to pentane. The processes apparently occur with partial coordination of H_2 ; no isomerisation is observed in the absence of H_2 .

Catalytic Coupling of Aromatics and Olefins by Homogeneous Palladium(II) Compounds under Oxygen

R. S. SHUE, *J. Chem. Soc., D, Chem. Commun.*, 1971, (23), 1510-1511

The coupling of aromatics such as C_6H_6 and olefins such as styrene, cyclohexene, etc., is catalysed by homogeneous Pd(II) complexes, especially $Pd(OAc)_2$ under mild O_2 pressure.

Kinetics and Mechanism of Hydrogenation of Cyclohexene Catalysed by Chlorotriphenylphosphinerhodium(I) in Benzene

S. SIEGEL and D. OHRT, *Inorg. Nucl. Chem. Letters*, 1972, 8, (1), 15-19

The kinetics and mechanism of the hydrogenation of cyclohexene catalysed by $Cl(PPh_3)_3Rh(I)$ in C_6H_6 were studied. The complex was slightly dissociated. At low alkene concentration and 1 atm. H_2 most of the catalyst is present as $Cl(PPh_3)_3RhH_2$ formed by dissociation of the complex followed by uptake of H_2 then of free PPh_3 .

ELECTRICAL AND ELECTRONIC ENGINEERING

An Improved Autogenic Hydrogen Reference Electrode

H. BINDER, A. KOHLING and G. SANDSTEDE, *Chem.-Ing.-Tech.*, 1971, 43, (19), 1084-1088

The electrode uses Raney Pt, and can be used without calibration for galvanostatic, potentiostatic, potentiodynamic and pulse measurements in strongly acidic or alkaline electrolytes. No additional H_2 is required.

The Effect of Corrosion, Electrical and Mechanical Loading on the Behaviour of Contact Materials

E. BAIER, *Verbindungstechnik*, 1971, 3, (3), 17-18

The properties and applications of electrical contact materials made of a number of precious metals and alloys including Au, Ag and Pt group metals are reviewed.

Report on British Corrosion Group Meeting

British Corrosion J., 1971, 6, (5), 192-193

The use of Pt/Ti for impressed current anodes and their performance, wear and efficiency were discussed. Tests indicated that wear rates of Pt are $\sim 1-2 \mu\text{g}/\text{amp hour}$. Reduction in life-time is probably due to acidity. An anode with 100μ in Pt should last 3-6 years at $100 \text{ amp}/\text{ft}^2$.

TEMPERATURE MEASUREMENT

Platinum Resistance Thermometers for Precise Measurements up to 1100°C

W. HEYNE, *Exp. Tech. Phys.*, 1971, 19, (2), 143-150

Improvements of the IPTS at $630-1064^\circ\text{C}$ were sought using Pt resistance thermometers for interpolation in place of Pt:Rh-Pt thermocouples. Low-resistance thermometers were made for 60 mm immersion having a 10 mm diam. ceramic insulator, with double wound coils of Pt wire 0.25, 0.3 and 0.5 mm thick enclosed in quartz tubes. After 40h the resistance change from thermal effects is $\pm 0.008 \text{ deg C}/\text{h}$ at 1060°C and less than ± 0.001 at 0°C . The thermal resistance changes did not depend on wire diameter unlike impurity effects. Only 0.5 mm wire had suitable precision as regards the latter.

NEW PATENTS

METALS AND ALLOYS

Nitrogen-free Platinum

E. I. DU PONT DE NEMOURS & CO.

British Patent 1,254,033

The manufacture of Pt powders, for use in metallising compositions and the production of printed circuits, which are relatively coarse-grained and free from N_2 , is described. Pt is precipitated by Zn from an aqueous PtCl_4 solution, HCl is added until no further reaction is observed and the precipitate is filtered off, washed and dried.

Relative Pressure Dependence of Chromel/Alumel and Platinum/Platinum-10% Rhodium Thermocouples

D. LAZARUS, R. N. JEFFERY and J. D. WEISS, *Appl. Phys. Lett.*, 1971, 19, (10), 371-373

Measurement of the relative thermal e.m.f.s of Chromel:Alumel and Pt:10% Rh-Pt thermocouples up to 7 kbar indicate a pressure correction for Pt couples of $0.57 \pm 0.03 \text{ deg C}/\text{kbar}$ from $600-1000^\circ\text{C}$. Systematic differences of unknown origin are found between pressure corrections measured with increasing and decreasing pressure.

Control of a Steel Ingot Intermediate Heating Furnace

H. KLAMMER, *Instrum. Prac.*, 1972, 26, (1), 31-33

Pt:Rh-Pt thermocouples are used to sense temperature in a comprehensive instrumentation system which controls the furnace temperature automatically. The system is designed with a view to computer control in the future.

High Precision Thermometry Using Industrial Resistance Sensors

A. THULIN, *J. Phys. E: Sci. Instrum.*, 1971, 4, (10), 764-768

Stability tests on glass-embedded and glass-bonded Pt wire 100 ohm sensors show that reproducibility in temperature measurement of a few millidegrees can be obtained when working below 150°C if the sensors are thermally cycled over the intended range of measurement prior to calibration.

Thermocouples for above 1500°C

E. D. ZYSK and A. R. ROBERTSON, *Instrum. Technol.*, 1971, 18, (11), 30-38

The use of thermocouples made of Pt, Rh, Ir, W, Re and other refractory metals in a variety of combinations is described for high temperature applications.

CHEMICAL COMPOUNDS

Hydride and Carbonyl Triphenylphosphine Derivatives of Ruthenium and Osmium

AMERICAN CYANAMID CO.

U.S. Patent 3,597,461

Pentacoordinate complexes of Ru and Os have the general formula $\text{M}(\text{CO})_{5-n}[\text{P}(\text{C}_6\text{H}_5)_3]_n$, where M is Ru, Os and n is 1,2. They are prepared by reacting the corresponding pentacarbonyls with triphenylphosphine. Dihydride compounds of formula $\text{MH}_2(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$ (M=Ru, Os) are also described.