

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Some Properties of Platinum, Palladium and their Alloys during Heating

E. I. RYTVIN, V. M. KUZ'MIN and A. E. RUDENKO, *Metalloved. term. Obrabot. Metal.*, 1968, (9), 71-72

The expansions of 25% Pd-Pt, 7% Rh-Pt, and 5% Rh-15% Pd-Pt after thousands of thermal cycles around 1300°C are tabulated. Results of annealing tests for 5h at 900 and at 1300°C confirm the high stability of Rh-Pt alloys compared to Pt or Pd, where grain growth occurs with increasing significance with temperature.

Volatilisation of Platinum-Ruthenium Alloys

E. I. RYTVIN and V. V. MALASHKIN, *Tsvetnye Metally*, 1968, (5), 80-81

Measurements of the volatility of 2, 5 and 10% Ru-Pt alloys heated in a resistance furnace in air at 1200, 1300, 1400, and 1500°C for 100h showed that increasing the Ru content causes a rise in the rate of volatilisation and that the addition of 5 and 10 wt% Rh does not alter this effect substantially. Microhardness measurements indicated that the main volatilising component was Ru. This was confirmed by volatility measurements in molten silicate medium, where the formation of volatile Ru oxides was prevented.

The Nature of the Coercive Force of Cobalt-Platinum Alloys in Well-regulated Conditions

YA. S. SHUR, L. M. MAGAT, G. V. IVANOVA, A. I. MITSEK, A. S. ERMOLENKO and O. A. IVANOV, *Fiz. Metall. Metalloved.*, 1968, 26, (2), 241-249

A high coercive force can be produced in well-regulated Co-Pt alloys with anisotropy constant $\approx 10^7$ erg/cm³ and in the single-phase state, where the magnetic reversal occurs by mixing of domains inside crystals of the ordered phase. Mixing is difficult when the phase boundaries are not well-regulated.

Superconductivity and Lattice Parameters in Face-centred Cubic Pt-W and Pd-W Solid Solutions

H. L. LUO, *J. less-common Metals*, 1968, 15, (3), 299-302

F.c.c. solid solutions of Pd and Pt were retained up to 44 and 67 at.% W respectively by adapting the liquid quenching technique to an arc furnace. Minima in the lattice parameter-composition

curves occurred at 10 at.% W-Pd and 18 at.% W-Pt. 26-44 at.% W-Pd and 28-67 at.% W-Pt were superconducting below temperatures which varied as a function of lattice parameter.

The Thermal Conductivity of 87% Platinum-13% Rhodium Alloy

J. MØLGAARD and W. W. SMELTZER, *J. less-common Metals*, 1968, 16, (3), 275-278

Values for K_{PR} , the thermal conductivity of 13% Rh-Pt, obtained by experiment fit the equation $K_{PR} = 0.607 - 0.092 (10^3/T)$, where T is in °K.

Thermodynamic Properties of Solid Rhodium-Palladium Alloys

K. M. MYLES, *Trans. Metall. Soc. AIME*, 1968, 242, (8), 1523-1526

Large positive deviations from ideal behaviour in the activities and free energies of formation, and positive enthalpies and entropies of formation of Rh-Pd alloys at 1575°K suggested a strong tendency towards phase separation in the solid solutions. Data was obtained from vapour pressure measurements made by the torsion-effusion method.

The Variation of Magnetoresistance in Copper-Palladium Solid Solutions in the Unordered and Ordered Atomic States

H. J. SEEMANN and G. SCHERER, *Z. Metallkunde*, 1968, 59, (10), 809-813

Room temperature measurements on Cu-Pd specimens coldworked, quenched from 800°C, and annealed showed that magnetoresistance varies as the square of the transverse magnetic field is decreased by cold working, and is increased by atomic ordering in Cu₃Pd but decreased in CuPd. Calculated and measured values were compared.

Strain Dependence of Exchange Interactions in Dilute PdFe Alloys and in Pure Pd

E. FAWCETT, D. B. MCWHAN, R. C. SHERWOOD and M. P. SARACHIK, *Solid State Commun.*, 1968, 6, (7), 509-513

Measurements of the magnetostriction and pressure dependence of Curie temperature in ferromagnetic 0.3, 1 and 3 at.% Fe-Pd indicate a positive strain-dependence of the exchange interaction between the conduction electrons and the local moments, contrasting with the negative strain-dependence value between the conduction electrons in pure Pd.

The Solubility of Carbon in Palladium and Platinum

R. H. SILLER, W. A. OATES and R. B. MCLELLAN, *J. less-common Metals*, 1968, **16**, (1), 71-73

Equilibrium solubilities of C in Pt and Pd at 875-1250°C were measured by a vapour transport technique. Pd dissolved large amounts of C, e.g. 0.7 wt% at 1200°C. Relative partial enthalpy and entropy of the C atoms showed that both solid solutions obey Henry's Law.

Magnetic Moments in Amorphous Palladium-Cobalt-Silicon Alloys

M. E. WEINER, *J. Metals*, 1968, **20**, (8), 99A

Studies of Pd_{80-x}Co_xSi₂₀ alloys, where x=3, 5, 7, 9, 10 and 11, at 1.8-300°K in fields up to 8.35 kOe showed that, for x≤9, Curie's Law holds with negligible permanent moments at room temperature. When x=10 or 11, alloys obeyed Curie's Law only above ≈200°K and had significant permanent moments at room temperature. In all cases the moments derived from Curie's Law were too high than moments of individual Co atoms would suggest. A model is proposed based on superparamagnetic clustering.

Electrical Resistivity of the Palladium-Deuterium System

G. BAMBAKIDIS, R. J. SMITH and D. A. OTTERSON, *Bull. Am. Phys. Soc.*, 1968, **13**, (7), 957, abstr. E2

Electrical resistivity measurements on Pd-D with up to 90 at.%D at 293, 77 and 4.2°K showed that at 4.2°K the resistivity increases at D/Pd≈0.68. These variations are less pronounced at the higher temperature. Possible models of this behaviour are discussed.

A Study of Some Palladium-Tin, Silver-Tin, and Palladium-Silver-Tin Alloys

I. R. HARRIS and M. CORDEY-HAYES, *J. less-common Metals*, 1968, **16**, (3), 223-232

Lattice spacings, magnetic susceptibilities and ¹¹⁹Sn Mössbauer isomer shifts for some Pd-Sn, Ag-Sn and Pd_{98-x}Ag_xSn alloys, where x varies from 0 to 98 at.%Ag, are consistent with a charge transfer model in which the Sn valence electrons are donated to vacant d-states in the Pd-rich alloys. In the Pd-Ag-Sn alloys there is a two-phase mixture of Pd₃Sn and solid solution, in the range 33-10% Pd, and this is reflected in an anomaly in the variation of the isomer shift with composition.

Investigation of Liquid Palladium-Tin Alloys

J. R. GUADAGNO and M. J. POOL, *J. phys. Chem.*, 1968, **72**, (7), 2535-2538

The heat of solution of Pd in liquid Sn was measured as a function of temperature and concentration in the dilute solution range at 700-800°K. The partial heat of solution, when compared to the heats of formation of PdSn, PdSn₂

and PdSn₄, shows similarities, indicating similar bonding in all cases with each Pd atom in the liquid surrounded by four Sn atoms. Density measurements on liquid 4% Pd-Sn show that a tetrahedral PdSn₄ molecule would have a Pd-Sn distance close to that of the intermetallic compounds.

On the Tungsten Compact by Low-temperature Sintering. III. Effects of Palladium Addition

H. ITO and H. FUKUNAGA, *J. Japan Soc. Powder Powder Metall.*, 1968, **15**, (3), 127-134

The sintering characteristics and mechanical and electrical contact properties of ≤5% Pd-W alloys were studied. 0.5% Pd-W gave dense compacts after 1h at >1000°C. Vickers hardness of 1-5% Pd-W sintered compacts had a maximum of 550 at 1000°C. Their transverse rupture strength was greater than that of Ni-P-W. Wear of ≤1% Pd-W contacts was similar to W with no observed transfer phenomena.

Thermal Expansion of Rhodium

R. R. PAWAR, *Curr. Sci.*, 1968, **37**, (8), 224-225

Measurements from 28 to 587°C on Rh enabled expressions to be derived for the lattice parameter and its variation with temperature, and by differentiation of this value the temperature dependence of coefficient of thermal expansion.

Magnetic Behaviour of Ni-Rh Alloys

H. COTTET, P. DONZÉ, J. ORTELLI, E. WALKER and M. PETER, *Helv. Phys. Acta*, 1968, **41**, (4), 398

Most results of measurements of magnetic susceptibility, of paramagnetic resonance of Gd, and of the speed of sound in Ni-Rh samples agree with a band model with exchange interaction. Ni₆₂Rh₃₈ doped with 0.8% Fe has a giant moment of ~12 Bohr magnetons. This drops to 2.5 μ_B/Fe atom in pure Rh. Magnetostatic measurements around Ni₆₂Rh₃₈ composition presented anomalies which are discussed.

A Calorimetric Study of the Rhodium-Tin System

R. V. MINER, P. J. SPENCER and M. J. POOL, *Trans. Metall. Soc. AIME*, 1968, **242**, (8), 1553-1554

The solution of Rh in dilute Rh-Sn at 700, 725, 750, and 775°K was very exothermic, -29,950 to -28,260 cal/g atom at infinite dilution. A sharp decrease in the heat of solution just before the solubility limit enabled the liquidus boundary to be established accurately at each temperature and also the heat of formation of RhSn₄ to be calculated.

Crystalline Phases in the Rhodium-Beryllium System. I. Rhodium Monoberyllide

A. A. KRUGLYKH, N. N. MATYUSHENKO and G. F. TIKHINSKII, *Ukr. fiz. Zh.*, 1968, **13**, (7), 1109-1113

Metallographic and X-ray diffraction studies

together with microhardness and optical measurements on 0-14% Be-Rh identified the isotropic phase RhBe with CsCl-type lattice, $a=0.2379$ nm, microhardness 13700 MN/m² and also the anisotropic phase RhBe₂ with density 6.8 g/cm³, microhardness 9300 MN/m².

Mechanical Relaxations in Polycrystalline Molybdenum, Tantalum and Iridium at High Temperatures and Low Frequencies

M. J. MURRAY, *J. less-common Metals*, 1968, **15**, (4), 425-435

Studies on poly- and monocrystalline specimens of Mo, Ta and Ir up to 2000°C using an inverted torsion pendulum with period ≈ 1 Hz indicated an internal friction peak at 1450°C in Ir, identified as a grain boundary peak. The activation energy associated with each relaxation was \approx activation energy for self-diffusion. The relaxation strength for Ir was large. Since the peaks were only present in polycrystalline specimens, the grain boundary type of relaxation is confirmed.

Resistivity of Some 5d Elements and Alloys Containing Iron

M. P. SARACHIK, *Phys. Rev.*, 1968, **170**, (3), 679-682

Resistivity-temperature studies on Fe-Ir, Fe-Os-Ir and Fe-Ir-Pt alloys showed that the resistivity due to Fe has a strong anomalous temperature dependence which is related linearly to Fe concentration and which changes gradually with alloy composition. No discontinuity in the resistivity behaviour of Ir-Fe was noticed. Anomalous scattering persists in Os-Ir alloys, where no magnetic moment resides on the Fe impurities.

F.I.M. Imaging of Solute Atoms in Dilute Binary Alloys

W. DUBROFF and E. S. MACHLIN, *Acta Metall.*, 1968, **16**, (11), 1313-1323

For >2 at.% W-, Pd-, Co-, Ni-, or Au-Pt, bright spots and vacant sites in field ion microscope images correspond to the lattice sites of solute atoms, while for ≤ 2 at.%, vacant site concentration exceeded solute concentration by ~ 1 at.%. The distribution of solute atoms is discussed.

CHEMICAL COMPOUNDS

Preparation and Semiconducting Properties of Platinum Antimonide

R. A. REYNOLDS, M. J. BRAU and R. A. CHAPMAN, *J. Phys. Chem. Solids*, 1968, **29**, (5), 755-770

PtSb₂ single crystals of the highest purity were prepared by horizontal zone refining and by Czochralski methods. Extrinsic carrier concentrations $\approx 10^{16}$ /cm³ and hole and electron

mobilities at $50-60^{\circ}\text{K}$ of $7,500$ and 6000 cm²/V sec were achieved. The semi-conducting properties of this compound are listed in full.

Crystal Chemistry and Electrical Transport Properties of Some Precious Metal Oxides

D. B. ROGERS and R. D. SHANNON, *Abstr. Papers, 156th Mtg, Am. Chem. Soc.*, 1968, (Sept.), INOR 43

Two rutile-type dioxides, RhO₂ and PtO₂, have been synthesised and crystals of RuO₂, OsO₂, IrO₂ and PdO have been grown. Single crystals of PdCoO₂ and Pt_{1-x}Co_{2-2x/3}O₄, where $0.6 \leq x \leq 0.8$, have been grown which are isostructural with CuFeO₂ and have twofold co-ordination of the precious metal by anions. Qualitative models of chemical bonding are related to occurrence, crystal chemistry and electrical behaviour of these materials.

Formation and Stability of the Platinum and Rhodium Oxides at High Oxygen Pressures and the Structures of Pt₃O₄, β -PtO₂ and RhO₂

O. MULLER and R. ROY, *J. less-common Metals*, 1968, **16**, (2), 129-146

Studies of the Pt-O and Rh-O systems at $p_{\text{O}_2} \leq 3500$ atm, $400-900^{\circ}\text{C}$ revealed the phases α -PtO₂, β -PtO₂, Pt₃O₄, Rh₂O₃, and RhO₂. Hexagonal α -PtO₂ has been described previously. CaCl₂-type β -PtO₂ and Na_xPt₃O₄-type Pt₃O₄ are black, highly insoluble solids, which are easily synthesised in these conditions. The reported tetragonal PtO and b.c.c. Pt₃O₄ were not encountered. RhO₂ has rutile structure and is a black, easily synthesised solid, highly insoluble even in hot aqua regia.

Ferrocene, Ruthenocene, and Osmocene. Iron, Ruthenium, and Osmium. Cobalt, Rhodium, and Iridium. Nickel, Palladium, and Platinum. Annual Surveys Covering the Year 1967

R. B. KING, *Organometal. Chem. Rev., Sect. B, Ann. Surv.*, 1968, **4**, (1), 67-80, 81-106, 107-136, 137-154

The cyanation of ruthenocene to C₈H₈RuC₅H₅CN is reported. The second section includes: the syntheses of Hg[Ru(CO)₂C₈H₈]₂, hexametallic Ru carbonyl derivations, cyclooctatetraene Ru carbonyl derivatives, Ru and Os pentacarbonyls, and olefin complexes of Ru and Os; reactions of Ru₃(CO)₁₂; carbonylation of Ru halides and the 1,2-cycloaddition reactions of C₈H₈ Ru(CO)₃. The third section includes: improved syntheses of Rh and Ir carbonyls, their stereochemistry and reactions; syntheses from carbonyl chlorides, of Rh and Ir complexes from fulvenes; Rh derivatives containing both triphenylphosphine and π -allyl ligands, and Rh and Ir complexes containing both π -cyclopentadienyl and organosulphur ligands. The fourth section includes:

Pd and Pt derivatives containing tertiary phosphine ligands; the preparation of Pt and Pd olefin complexes; square planar Pt(II) complexes; π -allylic Pd derivatives, and methyl derivatives of Pt.

The Structure of IrBr₃ and the Causes of Defect-order Phenomena in Noble Metal Halides Crystallised in Layer Structures

K. BRODERSEN, G. THIELE, H. OHNSORGE, I. RECKE and F. MOERS, *J. less-common Metals*, 1968, **15**, (3), 347-354

IrBr₃ has a strongly defect-ordered layer structure of the AlCl₃- or CrCl₃-type with a monoclinic crystal and lattice parameters $a=6.30$, $b=10.98$, $c=6.34\text{\AA}$, $\beta=108.7^\circ$. The defect arrangement is caused by stacking modifications of the metal layers.

Part III. Mechanism of the Formation of an Iridium Complex of Molecular Nitrogen

J.-Y. SUN, *Diss. Abstr. B*, 1968, **28**, (11), 4482-4483

A mechanism for the formation of a complex between Ir and N₂ is proposed.

Iridium Complexes of Molecular Nitrogen

J. P. COLLMAN, M. KUBOTA, F. D. VASTINE, J.-Y. SUN and J. W. KANG, *J. Am. Chem. Soc.*, 1968, **90**, (20), 5430-5437.

A study of the preparation of N₂ complexes with ClCO(Ph₃P)₂Ir and azides, including the reaction mechanism, the effect of using different azides, central metals and ancillary ligands, and the properties of the N₂ complex.

Part I. The Synthesis of Metal-Metal Bonds via Iridium and Rhodium Carbonyl Anions. Part II. The Synthesis and Properties of Acyl Isocyanate Complexes of Iridium and Rhodium

F. D. VASTINE, *Diss. Abstr. B*, 1968, **28**, (11), 4483

Previously unknown Ir and Rh carbonyl anions were synthesised and complexed to post-transition metal halides by metal-metal bonding. Complexes were characterised and their oxidising abilities were examined. The first known acylisocyanate metal complexes were synthesised from a novel Ir compound of N with acylisocyanate.

A New Type of Osmium—Post-transition Metal Complex Containing Four Metal Atoms

C. W. BRADFORD and R. S. NYHOLM, *Chem. Commun.*, 1968, (15), 867-868

Complexes containing four metal atoms were prepared by oxidising Os₃(CO)₁₂ with co-ordinated AuCl or AuBr. The red products are monomeric CHCl₃ and have spectra consistent with a linear arrangement of Au-Os-Os-Os. They do not conduct electricity. See comment on page 22 and succeeding abstract.

The Preparation and Vibrational Spectra of Compounds of the Type M(CO)₄(HgX)₂

C. W. BRADFORD, W. VAN BRONSWYK, R. J. H. CLARK and R. S. NYHOLM, *J. chem. Soc. (A), inorg. phys. theor.*, 1968, (10), 2456-2463

Ru(CO)₄(HgX)₂, (X=Cl or Br) and Os(CO)₄(HgX)₂, (X=Cl, Br or I) were prepared and their i.r. and Raman spectra were recorded at 2200-1900 and 700-70 cm⁻¹. All the compounds are monomers with cis-octahedral structures. Their spectra are compared with those of Fe(CO)₄(HgX)₂ and other M(CO)₄L₂ molecules.

Binuclear Nitrido-complexes of Ruthenium

M. J. CLEARE and W. P. GRIFFITH, *Chem. Commun.*, 1968, (21), 1302

Tests indicated that the reaction of [Ru(NO)X₅]²⁻ where X is Cl or Br, in complexes with HCHO or stannous halides yields compounds whose K salts are K₂[Ru₂^{IV}NX₆(H₂O₂)] with a linear Ru-N-Ru bridge. These are the first reported nitrido-complexes of Ru and join the small group of transition metal μ -nitrido-complexes. Spectra and diamagnetism of the new compounds are discussed.

ELECTROCHEMISTRY

Fluctuations of Overpotential at Metal Cathodes and Changes in Surface Concentration of Hydrogen Atoms

M. N. HULL and F. A. LEWIS, *Trans. Faraday Soc.*, 1968, **64**, (9), 2472-2475

Fluctuation of the total apparent H₂ overpotential at platinised Pt cathodes at low current density were correlated with irregular changes of the H₂ content of the electrode surface. The comparative lack of fluctuations at palladised Pd cathodes was attributed to H₂ absorbed in the Pd lattice.

Adsorption of Hydrogen on Hydrogenation Catalysts in Solution. I. Heat of Adsorption of Hydrogen on Pt Black in H₂SO₄ Solution

YU. A. PODVYAZKIN and O. R. SERGUTKINA, *Zh. fiz. Khim.*, 1968, **42**, (7), 1740-1743

H₂ adsorption on Pt in H₂SO₄ solution was studied from charging curves. Heats of adsorption were calculated for surface coverage ranging from 90 to 5%. Data agree with previously reported work on smooth and platinised Pt.

Electrochemical Behaviour of Titanium-Platinum Alloys in Processes of Anodic Oxidation. II. Relation of the Electrochemical Behaviour of Ti-Pt Alloys in H₂SO₄ Solutions to their Chemical Composition and Structure

E. G. KUZNETSOVA, T. I. BORISOVA, V. I. VESELOVSKII, and K. P. MARKOVICH, *Elektrokhimiya*, 1968, **4**, (8), 899-906

Kinetics and selectivity of anodes for the forma-

tion of O_2 , $H_2S_2O_8$ and O_3 were studied on 1, 2, 5, 10, 25, 40, 60, and 80 wt% Pt-Ti alloys in 12.3 N H_2SO_4 at 0 to $-30^\circ C$. The rate of $H_2S_2O_8$ synthesis rises with Pt content and is greatest for 60–80 wt.% Pt-Ti at 3.4V and $-30^\circ C$. Yield of $H_2S_2O_8$ is high on $<1-2\%$ Pt-Ti alloys with α -solid solutions but is less on metallides even where they incorporate 60–80 wt% Pt. This is accounted for by the presence of separate Pt oxides in the mixture of Ti and Pt oxides at the surface of the anodes made from α -solid solution alloys.

Specific Activity of Platinum for the Electrocatalytic Oxidation of Acetate

R. WOODS, *Electrochim. Acta*, 1968, **13**, (10), 1967–1972

The specific activity for the electrocatalytic oxidation of acetic acid and acetate ions for various forms of Pt electrode (Pt foil, precipitated Pt black, electrodeposited Pt, Pt-Pb and Raney Pt) is independent of the mode of preparation over a 10^3 change in surface roughness. Apparent changes in specific activity were observed on depletion of acetate ion and increased acidity in the micropores.

ELECTRODEPOSITION AND SURFACE COATINGS

Platinised Titanium as Insoluble Anode Material

J. W. KÜHN-VON BURGSDORFF, *Galvanotechnik*, 1968, **59**, (8), 659–666

A review of the uses of Pt/Ti anodes, which are used increasingly in acid precious metal and acid Au plating baths, and also in H_2SO_4 baths for hard Cr plating. They are also used as auxiliary anodes for Ni and Cr plating of hollow parts.

LABORATORY APPARATUS AND TECHNIQUE

Preparation and Fabrication of Ceramic Electric Leads

P. P. BUDNIKOV, F. YA. KHARITONOV, B. P. GOLUBEV and S. N. SMIRNOV, *Ogneupory*, 1968, **33**, (3), 31–33
Electrodes were made by embedding stretched 0.3 mm Pt or Rh-Pt wires under pressure in a mould containing a corundum-microlite mixture, hardening them at room temperature, drying to remove the binder, and firing directly over a flame at $1750^\circ C$ to give a hermetic seal between metal and ceramic. When used to determine concentrations of KCl, NaCl, Na_2SiO_3 , etc., up to $400^\circ C$, 300 kg/cm², they lasted 200h at varying temperatures and pressures.

HETEROGENEOUS CATALYSIS

Catalytic Activity of Platinum Black

A. N. MAL'TSEV, N. I. KOBOZEV and L. V. VORONOVA, *Zh. fiz. Khim.*, 1968, **42**, (8), 1967–1970

Measurements during the hydrogenation of C_6H_{12} -I in relation to the amount of poison adsorbed on the surface of Pt black saturated with H_2 showed that two types of centre exist for hydrogenation with activities differing ~ 5 times.

Catalytic Oxidation of Hydrogen on Platinum Studied by the ESR Method

V. V. SHALYA, R. A. KASHIRINA, R. L. KANINSKAYA and YA. B. GOROKHOVATSKII, *Dokl. Akad. Nauk SSSR*, 1968, **180**, (6), 1408–1410

Condensed products of the H_2 - O_2 reaction on Pt were studied by the ESR method for various temperatures and pressures of the reaction mixture. The shape of the Pt rod affected results, indicating the progress of the heterogeneous-homogeneous mechanism.

Catalytic Decomposition of Methanols over Platinum and Ruthenium

D. W. MCKEE, *Trans. Faraday Soc.*, 1968, **64**, (8), 220C–2212

The decomposition of CH_3OH , CH_3OD and CD_3OH at $70-250^\circ C$ over Pt yielded mainly CO and H_2 , the rates showing a marked kinetic isotope effect, whereas Ru was much more active giving high yields of CH_4 . Above $155^\circ C$ addition of Ru to Pt increased its activity until at 30% Ru an abrupt change to the methanation mechanism took place. Mechanisms and information on the composition of the catalyst surface are discussed.

Study of the Regularity of Crystallisation of Platinum on Supports. I. Relation of the Dispersion and Activity of Platinum, Supported on Aluminium Oxide, to the Surface Concentration and Properties of the Supports

N. M. ZAIDMAN, V. A. DZIS'KO, A. P. KARNAUKHOV, N. P. KRASILENKO, N. G. KOROLEVA and G. P. VISHNYAKOVA, *Kinet. Kataliz*, 1968, **9**, (4), 863–869

Studies of the dispersion of 0.1–2.0 wt.% Pt on Al_2O_3 samples with various structures and specific surfaces in conditions similar to those of the preparation and use of reforming catalysts showed a linear relationship between the inverse size of dispersion, expressed as H/Pt, and the surface concentration of Pt. This relation has a coefficient of proportionality characterising the ability of Pt to form aggregates or to crystallise on the surface of the support. This general relation also applies to Ag/corundum. All studied catalysts had the same specific activity for cyclohexane dehydrogenation. Results explain the existence of optimum concentrations of Pt in Pt/ Al_2O_3 reforming catalysts.

Hydrocracking and Diffusion of Pure Compounds on Mordenite Catalysts

R. BEECHER, A. VOORHIES and P. EBERLY, *Ind. engng Chem., prod. Res. Dev.*, 1968, 7, (3), 203-209
Pd on Al-deficient H-mordenite is ~ 4 times more active than Pd/H-mordenite for cracking $n\text{-C}_{10}\text{H}_{22}$ and decalin at 450 psig, 450-610°F. Activation energies are 44 and 33 kcal/mole for $n\text{-C}_{10}\text{H}_{22}$ and 25 kcal/mole for decalin. Pure $n\text{-C}_{10}\text{H}_{22}$ is more reactive than pure decalin but in approximately even mixtures the latter is converted while $n\text{-C}_{10}\text{H}_{22}$ is not. The increased activity of Al-deficient H-mordenite is partly due to its lower diffusion resistance.

Dehydrogenation of Monocyclic Naphthenes over a Platinum on Alumina Catalyst without Added Hydrogen

A. W. RITCHIE and A. C. NIXON, *Ibid.*, 209-215
Pt/Al₂O₃ showed good selectivity and catalytic stability in the dehydrogenation of cyclohexane and of its methyl and ethyl derivatives at 10 atm, 840-1200°F. The alkyl substituents increased the reaction rate by an amount depending on their positions in the ring, the stereochemistry and the reaction temperature.

Catalytic Properties of the Platinum Group Metals and their Alloys Based on Palladium

D. V. SOKOL'SKII, R. G. DAVLESUPOVA, A. M. KHISAMETDINOV and F. B. BIZHANOV, *Kinet. Kataliz*, 1968, 9, (5), 1080-1085

Studies of Raney catalysts of Pt group metals and their Pd-based alloys during hydrogenation of dimethylethynylcarbinols showed the effects of catalyst and of solvent on the kinetics and direction of the reaction. Charging curves during anodic polarisation by organic substances showed the ability of catalysts to adsorb H₂. The inactivity of Ru, Ir, Os, and Re is due to their insignificant adsorption of H₂. X-ray studies allowed comparison of catalyst surfaces during H₂ and air adsorptions. Not all of a catalyst surface is accessible to H₂.

Preparation of Highly Dispersed Catalytic Metals. Platinum Supported on Silica Gel

H. A. BENESI, R. M. CURTIS and H. P. STUDER, *J. Catalysis*, 1968, 10, (4), 328-335

The dispersion of Pt in catalysts prepared by ion exchange of Pt-ammine cations with SiO₂ gel support, followed by reduction, was much greater than that in similar catalysts prepared by impregnation with aqueous H₂PtCl₆. H₂ chemisorption, X-ray diffraction and electron metallography methods showed that the Pt is in the form of finely dispersed 15 Å crystallites.

On the Selectivity of Platinum Catalysts

M. BOUDART, A. W. ALDAG, L. D. PTAK and J. E. BENSON, *J. Catalysis*, 1968, 11, (1), 35-45

Initial rates of reaction of neopentane were measured at 300°C, 1 atm, H₂: neopentane = 10

on Pt powder and on Pt/SiO₂, Pt/C, Pt/ $\eta\text{-Al}_2\text{O}_3$, and Pt/ $\gamma\text{-Al}_2\text{O}_3$. The Pt dispersion, defined as % Pt atoms at the surface, varied from 3×10^{-2} for the powder to > 70 for the supported catalysts. Neopentane underwent concurrent isomerisation to isopentane and hydrogenolysis to isobutane and CH₄. Selectivity for isomerisation varied by a factor of 100 for the catalysts studied. Selectivity of supported catalysts increased with increasing catalyst pretreatment temperature from 425 to 900°C and a mechanism is suggested for this behaviour.

Study of Supported Catalysts by the Exoelectronic Emission Method. IX. Zinc Oxide with Additions of Platinum, Silver and Gold. Investigation of Secondary Electron Multiplication

T. S. USTINOVA, and I. V. KRYLOVA, *Zh. fiz. Khim.*, 1968, 42, (8), 2086-2089

The intensity of exoelectronic emission at the surface of Pt/ZnO, Ag/ZnO and Au/ZnO, which reaches a maximum at 140-150°C, was not reduced by previous treatment in vacuum at 400°C. Preliminary adsorption of O₂ and H₂ at 200-300°C raised the intensity of emission at room temperature. Exoelectrons were localised due to chemisorption of O₂ and hydroxyl on the surface.

Chemical Transformations of Diols and Cyclic Ethers. XXVI. Investigation of the Conversion of 2,4-Dialkyl-substituted Oxetanes in the Presence of Platinum Catalyst by the Microreactor Technique

M. BARTOK, K. KOVACS and N. I. SHUIKIN, *Acta Chim. Acad. Sci. Hung.*, 1968, 56, (4), 393-404

Conversions of 2-methyl-4-ethyl-, 2-methyl-4-*n*-butyl- and 2-methyl-4-cyclohexyl-oxetanes over Pt/thermolite and Pt/C in H₂ and He at 200-350°C yielded mainly isomeric ketones by breaking of the two C-O bonds (60-70%) and olefins and corresponding aldehydes by thermal decomposition (30-40%), the relative amounts depending on catalyst activity, temperature and substituent effects. Pt/C was the more active.

Kinetics of the Dehydrogenation of Cyclohexene on Palladium at Pressures below 10⁻³ torr

V. SHIMULIS, I. KONOVALOVA and G. EUNICE VERA, *Zh. fiz. Khim.*, 1968, 13, (7), 1667-1672

A new method of studying the kinetics of dehydrogenation at initial pressures of 1.10^{-5} to 1.10^{-3} torr, including reduction of the catalytic activity of Pd during the reaction, confirmed the stepwise nature of the reduction of cyclohexane. Study of the $\sim 50^\circ\text{C}$ stage below 1.10^{-3} torr established that the kinetics below 3.10^{-4} torr can be explained by the Langmuir-Hinshelwood equation. The surface of Pd is heterogeneous due to its lattice structure.

Investigation of the Conversions of Cyclohexadiene-1,3 and Cyclohexadiene-1,4 in the Presence of Rhodium Catalysts

L. KH. FREIDLIN and I. L. POPOVA, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, (7), 1514-1521

During room temperature conversion of cycloolefins over Rh black and Rh/C, cyclohexadiene-1,3 reacts before cyclohexadiene-1,4 and cyclohexene is formed. The direction of conversion of cyclohexadiene isomers depends on the amount of H₂ at the catalyst surface. Hydrogenation and disproportionation of cyclohexadiene-1,3 occur together at ordinary pressures but only at reduced pressures with cyclohexadiene-1,4. Cyclohexadiene-1,3 is disproportionated and dehydrogenated in N₂. Cyclohexane is hydrogenated more easily and is dehydrogenated less easily than the cyclohexadienes and is probably not disproportionated. Disproportionation is not observed when the cycloolefins cannot be dehydrogenated.

Catalytic Activity of Rhodium and Ruthenium in the Hydrogenolysis of Ethane

G. K. STAROSTENKO and T. A. SLOVOKHOTOVA, *Vest. moskov. Univ., Ser. II, Khim.*, 1968, 23, (5), 106-108

3.14% Rh/SiO₂ and 3.14% Ru/SiO₂ catalysts with wide pores were studied during the hydrogenolysis of C₂H₆ and it was found that the texture did not affect the activation energy and the orders of the reaction with respect to C₂H₆ and H₂.

Study of the Catalytic Properties of Iridium Supported by Alumina. I. Textural Study by Adsorption of Gas and Electron Microscopy

J. P. CONTOUR and G. PANNETIER, *Bull. Soc. chim. France*, 1968, (9), 3591-3596.

The surface area of Ir/Al₂O₃ was measured using the physical adsorption of N₂ and A at 77°K, and the activity of the metal surface using chemisorption of H₂ at 473°K. Agreement between those results and electron microscopy was satisfactory and the variation of metallic area was studied as a function of Ir content.

HOMOGENEOUS CATALYSIS

Homogeneous Catalytic Hydrogenation and Isomerisation of Olefins with Dichlorobis(triphenylphosphine) platinum(II) - Tin(II) Chloride Catalyst

R. W. ADAMS, G. E. BATLEY and J. C. BAILAR, *Inorg. nucl. chem. Lett.*, 1968, 4, (8), 455-458

Terminal double bonds proved to be the most favoured for hydrogenation with PtCl₂(Ph₃P)₂ and SnCl₂, and dienes with two terminal double bonds yielded small quantities of saturated material. Isomerisation occurred with dienes but

conjugation was inessential for hydrogenation. Formation of a metal hydride-olefin intermediate is proposed in which an unusually strong metal-olefin bond would inhibit hydrogenation.

Arylation, Methylation, and Carboxyalkylation of Olefins by Group VIII Metal Derivatives

R. F. HECK, *J. Am. Chem. Soc.*, 1968, 90, (20), 5518-5526

The reaction of aryl, methyl and carboxyalkyl derivatives of Pd, Rh and Ru with olefins is insensitive to O₂ and H₂O and can be made catalytic by employing CuCl₂ as reoxidant. It offers a useful method for a wide range of organic syntheses. See the following group of abstracts.

The Arylation of Allylic Alcohols with Organopalladium Compounds. A New Synthesis of 3-Aryl Aldehydes and Ketones

Ibid., 5526-5531
Aryl-Pd salts were prepared in situ from aryl-Hg salts and a Pd salt and reacted with primary or secondary allylic alcohols to produce 3-aryl aldehydes and ketones.

Allylation of Aromatic Compounds with Organopalladium Salts

Ibid., 5531-5534
Moderate yields of allylaromatic derivatives were obtained from allylic halides by the same method.

The Palladium-Catalysed Arylation of Enol Esters, Ethers and Halides. A New Synthesis of 2-Aryl Aldehydes and Ketones

Ibid., 5535-5538
Other uses for this reagent are the preparation of arylacetaldehyde derivatives, arylacetaldehyde enol ester derivatives, aryl ethylenes and stilbenes from aldehyde enol esters, stilbenes from vinyl ethers and halides and α -aryl ketones from ketone enol esters. Yields are generally low, but the reaction is simple and convenient.

Aromatic Haloethylation with Palladium and Copper Halides

Ibid., 5538-5542
Aryl mercuric halide and Li₂PdCl₄ reacted with olefins in the presence of Cu halides to form 2-arylethyl halides, a convenient method for introducing 2-haloethyl groups into aromatic systems.

The Addition of Alkyl- and Arylpalladium Chlorides to Conjugated Dienes

Ibid., 5542-5546
1-Arylmethyl and 1-alkyl- π -allyl-PdCl₂ dimers were formed in low to moderate yields when conjugated dienes were reacted with aryl- and

alkyl-Pd chlorides prepared in situ from aryl and alkyl Hg or Sn salts and Li_2PdCl_4 . A catalytic synthesis of arylbutenyl acetates from a conjugated diene, an arylmercuric salt and Pt tetraacetate with catalytic amounts of Pd acetate is also reported.

A Synthesis of Diaryl Ketones from Arylmercuric Salts

Ibid., 5546-5548

Arylmercuric chlorides react with CO and Pd or Rh halide catalysts to form diaryl ketones in fair yields.

Vinyl Acetate from Ethylene in the Liquid Phase with Palladium Salts as Catalysts

H. KREKELER and H. SCHMITZ, *Chem.-Ing.-Tech.*, 1968, **40**, (16), 785-788

PdCl_2 , CuCl_2 and O_2 were used in a pilot plant for the production of vinyl acetate. CH_3CHO formed as a by-product provided enough CH_3COOH for the vinyl acetate production. Capacity was 50 t/month.

Exchange of Molecular Nitrogen with Nitrogen of the Coordination Sphere of Nitrogenyl Ruthenium

A. K. SHILOVA, A. E. SHILOV and Z. N. VOSTROKNUTOVA, *Kinet. Kataliz.*, 1968, **9**, (4), 924-926

IR spectra of $\text{RuN}_2(\text{H}_2\text{O})_2\text{Cl}(\text{THF})$, referred to as RuL_5N_2 , after thermal decomposition in $\text{C}_2\text{H}_6\text{O}$ in an atmosphere of N_2^{16} , indicated exchange between N_2 of the co-ordination sphere of Ru with atmospheric N_2 . This is explained by the reaction of RuL_5 , formed during decomposition of RuL_5N_2 ; with dissolved atmospheric N_2 to give again RuL_5N_2 . This is confirmed by the decreased rate of decomposition of the complex when the pressure of dissolved N_2 increases.

Molecular Structure of the Hydrogenation Catalyst Hydrido-chlorotris(triphenylphosphine)-ruthenium (II)

A. C. SKAPSKI and P. G. H. TROUGHTON, *Chem. Commun.*, 1968, (20), 1230-1231

The crystal and molecular dimensions of $\text{RuClH}(\text{PPh}_3)_3$, the most active homogeneous catalyst yet known, were calculated using 3-dimensional X-ray analysis.

Oxidation of Olefins by Ferricyanide Using Osmium Tetroxide Catalyst

J. S. MAYELL, *Ind. engng Chem., prod. Res. Dev.*, 1968, **7**, (2), 129-136

Qualitative and selective production of glycols from olefins in aqueous alkaline solutions used OsO_4 as homogeneous catalyst and $\text{K}_3\text{Fe}(\text{CN})_6$. During the reaction Os^{8+} was converted to Os^{6+} and $\text{Fe}(\text{CN})_6^{3-}$ to $\text{Fe}(\text{CN})_6^{4-}$. Os^{8+} and $\text{Fe}(\text{CN})_6^{3-}$ were regenerated electrochemically. The reaction mechanism was studied.

FUEL CELLS

The Performance of Direct Ammonia Fuel Cells

E. L. SIMONS, E. J. CAIRNS and D. J. SURD, *Extended Abstr., Electrochem. Soc.*, 1968, (October), abstr. 349

$\text{NH}_3\text{-O}_2$ and $\text{NH}_3\text{-air}$ fuel cells were tested with Pt black and Pt/graphite electrodes at 140, 120, 80, 60, and 25°C. Continuous operation at increasing load showed that at 800 mA/cm² at room temperature operation is possible using Pt black electrodes with no external heat source for starting. Results of runs at 120°C using 54% KOH electrolyte and Pt/graphite are plotted.

Improved Electrocatalysts for Ammonia Fuel Cell Anodes

D. W. MCKEE, A. J. SCARPELLINO and I. F. DANZIG, *Ibid.*, abstr. 350

The performance of 21.3% Ir-Pt and 51% Ir-Pt electrodes in the form of Adams-type blacks bonded with Teflon and of Ir and Pt co-deposited on graphite and B_4C in 54% KOH solution up to 140°C were compared with a standard Pt black electrode. Plots of results indicate that Ir additions considerably improve electrode activity. The mechanism is discussed. Ir appears to be much more active than the other Pt metals for the dissociation of NH_3 at elevated temperatures.

ELECTRICAL AND ELECTRONIC ENGINEERING

Hermetic Seals by Thick-film Techniques

G. R. COLE, *Solid State Technol.*, 1968, **11**, (8), 43-46

The best combination of materials appeared to be Pt-Au metallisation over a glass or glass-ceramic crossover. Pt-Pd on glass ceramic had higher adhesive strength and all the layers could be fired at once but had slightly less resistance to thermal cycling and was sensitive to processing conditions. Pd-Au and Pd-Ag made good seals but were not subjected to low temperature cycling. Polymer sealants may not be as reliable but are cheaper.

TEMPERATURE MEASUREMENT

Pressure Effect on the Platinum versus Platinum 10% Rhodium Thermocouple

P. M. BELL, J. L. ENGLAND and F. R. BOYD, *Carnegie Inst., Wash., Yr Bk*, 1968, **66**, 545-547

Corrections to the values recorded by Pt: 10% Rh-Pt thermocouples were determined for pressures up to 9 kbar at 20, 185, 305, and 509°C and amount to >3°C at 509°C, 5 kbar.

The Effect of Reactor Exposure on Thermocouple Materials

N. F. PRAVDYUK, A. N. IVANOV and K. P. DUBROVIN,
Atomnaya Energiya, 1968, **25**, (3), 233-235

Neutron irradiation causes slight changes in the thermo-e.m.f. of thermocouple materials due to the formation of radiation defects. Tests using up to $\approx 10^{20}$ neutron/cm² on 60% Au-Pd, Pt,

13% Rh-Pt, and base metal alloys showed that after annealing there is a slight increase in thermo-e.m.f. for 60% Au-Pd and a slight decrease for Pt and 13% Rh-Pt. Results are tabulated and displayed graphically. Annealing reduces the number of defects and hence errors in thermocouples exposed to radiation at high temperatures may be lower than those at lower temperatures.

NEW PATENTS

METALS AND ALLOYS

Alloy

INTERNATIONAL BUSINESS MACHINES CORP.

British Patent 1,125,690

Magnetic thin films for computer storage elements may be made from an alloy of 69.9-80 at.% Ni, 18-20.2 at.% Fe and 1-12 at.% Pd.

Finely Divided Noble Metal Alloys

E. I. DU PONT DE NEMOURS & CO.

U.S. Patent 3,390,981

Alloys of two noble metals selected from Ag, Au, Pt and Pd are produced by mixing solutions of salts of these metals and then reducing the mixture (e.g. of Pd and Ag nitrates) to give an alloy in finely divided form. H₃PO₂ is a suitable reducing agent.

A Niobium-Tungsten Alloy

BIRMINGHAM SMALL ARMS CO. LTD

U.S. Patent 3,395,012

An alloy consists of at least 30% Nb, 10-25% W, up to 40% Ta, and 0.1-10% of at least one element selected from Ru, Os and Ir.

Laminated Metal Plates and Strip

JOHNSON, MATTHEY & CO. LTD

German Patent 1,271,494

The bonding of Pt or Pt alloy to Ti, Ta, Nb, V or Zr mechanically, especially to produce electrodes, is improved by using pressures of 80-800 kp/cm² at 800-950°C.

Fountain Pen Ruthenium Alloy

W. C. HERAEUS G.m.b.H.

German Patent 1,276,332

A ternary alloy for nib tips comprises 10-40% Re, 15-45% Ru and 15-50% W.

CHEMICAL COMPOUNDS

Trimeric Ruthenium Carbonyl

LONZA LTD

U.S. Patent 3,387,932

[Ru(CO)₄]₃ is prepared by reacting a basic Ru salt and a carboxylic acid or Ru acetylacetonate

with CO at elevated temperature and pressure in the presence of MEK or a lower alcohol.

ELECTROCHEMISTRY

Porous Electrodes for Electrochemical Cells

GULF GENERAL ATOMIC INC.

British Patent 1,124,362

Metal porous electrodes are produced by shaping a mixture of metal particles, e.g. Ni, with C particles using heat and pressure and then removing the C by electrolysis. The porous Ni matrix is impregnated using a thermally unstable organic salt of a Pt metal.

Anodes for Electrolytic Cells

TSURUMI SODA CO. LTD

British Patent 1,128,136

Anodes for the electrolysis of halide compounds (e.g. NaCl) are produced from an alloy of 3-80% Pd and 97-20% Rh or of 5-80% Pd and 95-20% Pt which is subjected to oxidative treatment at 180-1350°C in an oxidising atmosphere, or electrolytic oxidation in a fused salt bath.

Electrocatalytic Surfaces

GENERAL ELECTRIC CO. (NEW YORK)

U.S. Patent 3,396,091

High electrocatalytic activity is produced by plating a Pt metal-base metal alloy from a common bath and then removing the base metal by etching.

ELECTRODEPOSITION AND SURFACE COATINGS

Metallising Compositions

E. I. DU PONT DE NEMOURS & CO.

U.S. Patent 3,385,799

Electroconducting areas are produced on non-conducting surfaces, especially ceramics, using a mixture of 30-90% noble metal alloy powder, dispersed in 10-70% of an inert liquid organic vehicle; the powder has 90% of the particles not greater than 5 microns in size and is made from two noble metals selected from Ag, Au, Pt and Pd.