

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Oxide Dispersion-strengthened Platinum

A. S. BUFFERD, K. M. ZWILSKY, J. T. BLUCHER and N. J. GRANT, *Internat. J. Powder Met.*, 1967, 3, (1), 17-26

Tension and stress rupture tests, and micro-structural examination of oxide dispersion-strengthened Pt alloys prepared by mechanical mixing or salt decomposition were used to determine the effects of Pt particle size from 2-20 μ , choice of dispersoid, Al_2O_3 , CeO_2 or ThO_2 , and volume fraction of dispersoid, v/o , on their high temperature properties. Best results are obtained using fine powder and salt decomposition, e.g. Pt powder, 1-2 μ , and ThO_2 , $v/o=12.5$, obtained by decomposition of $Th(NO_3)_4$, has a stress rupture life of 100 h at 6400 psi, 1100°C and at 2800 psi, 1300°C.

A Study of the Eutectics in the Systems Platinum-Carbon and Iridium-Carbon

S. K. RHEE, *Diss. Abs. B*, 1966, 27, (6), 1963

A study of the Pt-C and Ir-C phase diagrams shows that the limited solubility of C in Pt and Ir gives rise to eutectic points at 16.8 ± 1.0 at. % C, $1705 \pm 13^\circ C$ and 29.0 ± 1.0 at. % C, $2150 \pm 22^\circ C$, respectively.

The $\beta \rightarrow \alpha$ Phase Change in a Uranium-Platinum-Niobium Alloy

W. J. KITCHINGMAN and K. M. PICKWICK, *J. Inst. Met.*, 1967, 95, (2), 38-43

Addition of Nb retards the rate of the $\beta \rightarrow \alpha$ transformation in U-Pt alloy and raises the point of maximum reaction rate to higher temperatures. It causes separation of the high-temperature C's in the TTT curves. Transformation kinetics suggest a thermally activated, diffusion-controlled process in C₁ and probably a bainitic reaction in C₂, where C₁ and C₂ are curves for 5 and 95% transformation. The tested U-0.35 at. % Pt - 1.56 at. % Nb alloy had structures similar U-1 at. % Pt. Electrical resistance tests were carried out at different rates of heating and cooling, and also for isothermal transformations between 480-630°C.

Determination of the Deformation, Connected with the Grain Boundaries during Elongation of Palladium in a Wide Range of Temperature

M. G. LOZINSKII and V. YA. FERENETS, *Fiz. Met. Metalloved.*, 1967, 23, (2), 293-299

The tendency of the grain boundaries of Pd to deformation under stress is slight at 20-400°C

but it increases as they weaken to 900°C. Recrystallisation develops at 1000°C and obscures mixing at grain boundaries. While subjecting Pd to tension, the amount and type of deformation can be estimated by photogrammetry.

Optical Properties and Fermi Surface of Palladium

G. A. BOLOTIN, M. M. KIRILLOVA, L. V. NOMEROVANNAYA and M. M. NOSKOV, *Ibid.*, (3), 463-471

Room temperature studies at 0.07-13 eV of porous Pd enabled a model of the band structure and Fermi surface of Pd to be constructed which agreed with data on electronic specific heat, galvanomagnetic effect, and de Haas-van Alphen effect, and showed that the optical properties of Pd could be interpreted within its frame.

Change of Electrical Resistance of Palladium Film Due to Adsorption of Carbon Monoxide

K. KAWASAKI, T. SUGITA and S. EBISAWA, *Surface Sci.*, 1967, 6, (3), 395-397

The relative change of the electrical resistivity of a thin Pd film increases linearly with the volume of CO adsorbed until this exceeds 6×10^{14} mol/cm², when the relationship no longer holds. Results show that for surface coverage $\theta < 0.5$, the number of conducting electrons β , immobilised by adsorption of one gas molecule, is two, indicating that CO is adsorbed in the bridge form; and for $\theta > 0.5$, β decreases to a minimum of 1.4 suggesting that the linear and bridge forms coexist.

Ordered Alloys of the Gold-Palladium System. II. Electron Diffraction Study on Evaporated AuPd₃ Films

Y. MATSUO, A. NAGASAWA and J. KAKINOKI, *J. Phys. Soc. Japan*, 1966, 21, (12), 2633-2637

Electron diffraction studies indicated the presence of the superlattice AuPd₃ in evaporated single crystal films of alloys with composition $\sim AuPd_3$ and detected the order-disorder transformation for ~ 80 at. % Pd-Au at $\sim 780^\circ C$. Superlattice reflections were weak but sharp, denoting reduced degree of order. This special nature of AuPd₃ was compared with other noble metal-Pd ordered alloys.

Effect of Deformation on Physical Properties of Gold-Palladium and Copper-Palladium Alloys

M. J. KIM, *Diss. Abs. B*, 1966, 27, (6), 1962

Studies show that the destruction of short range

order in certain Cu-Pd and Au-Pd alloys by cold working lowers the resistivity. The recovery of the deformed alloys by isothermal and isochronal annealing showed stages similar to those observed in the pure metal. The activation energy, order of reaction and relaxation times for the annealing process were also determined.

A Neutron Diffraction Study of the α -Phase in the Palladium-Gold-Hydrogen and Palladium-Gold-Deuterium Systems

A. J. MAELAND, *Abs. Papers, 153rd Meeting, Am. Chem. Soc.*, 1967, (Apr.), R 189

Alloying of Pd with Au increased the H or D concentration in the α -phase without using high temperature or pressure. Neutron diffraction studies showed that both H and D are located in the octahedral positions of the f.c.c. lattice. It is assumed that they also occupy these positions in the α -phase of Pd-H and Pd-D.

Mixing Behaviour of Palladium Alloys of the Intermediate and Substituted Crystal Types

H. BRODOWSKY, *Z. Naturf.*, 1967, **22a**, (1), 130-137

Deviation from ideal behaviour of the H-Pd and Ag-Pd systems, which have analogous excess potentials, is due to elastic interactions at low concentrations and also to filling of the 4d- and 5s- electron bands of Pd at higher concentrations. Activity measurements indicate a misfit energy of 950 cal/mole, and an energy of attraction of -660 kcal/mole pair for 50% Ag-Pd at 700°C. A density state of 0.9 electrons/eV is calculated for the 5s-band, which agrees well with the value obtained from H₂ adsorption studies.

Formation of Alloys at Room Temperature

H. HIRSCH, *Nature*, 1967, **213**, (5078, Feb. 25), 793-794

Ag and Cu foils are immersed in 0.002 M solutions of Na₂PdBr₄, Na₂PtBr₄ and Na₂Au(S₂O₃)₂, and after one or two days metallic skins on the foil can be stripped off easily, which contain >50 at.% of the less noble metal. Cu-Ag alloys cannot be obtained and the Au-Ag lattice parameters cannot be measured.

Properties of Alloys of Silver with Small Additions of Palladium and Cadmium

N. L. PRAVOVEROV and L. A. TRIBUNSKAYA, *Izv. Akad. Nauk S.S.S.R., Metally*, 1967, (1), 156-159

Additions of Pd and Cd, not exceeding 1%, to Ag increase its limits of stability by 17-18% and decrease its reaction with gases at high temperature. Pd additions contribute a greater increase of specific electrical resistance and a greater decrease of temperature coefficient of electrical resistance in the alloy than do Cd additions.

Theory of the Magnetic Properties of Dilute Palladium-Iron Alloys

S. DONIACH and E. P. WOHLFARTH, *Proc. Roy. Soc.*, 1967, **296A**, (1447), 442-456

Studies of the dynamic properties of dilute alloys of Fe in Pd and Pd alloys, based on a model in which local spin on the Fe atom magnetises the surrounding matrix via a coupling of strengths, led to prediction of the spin wave spectrum at long wavelengths and to analyses giving a consistent value for J of 0.15 ± 0.02 eV. Energy of the long wave optical mode is predicted to be proportional to Fe concentration and to be 0.015 eV for 1% Pd-Fe.

On the Possibility of Reducing the Tendency of Steel to Flake Formation by Means of Small Additions of Palladium

V. I. ARKHAROV, A. A. KRALINA, L. I. KVATER and P. V. SKLYUEV, *Izv. Akad. Nauk S.S.S.R., Metally*, 1967, (1), 105-111

Investigation of the addition of 0.4-0.5% Pd to a medium alloy steel to give a continuous series of solid solutions shows that the resulting increase in diffusion of dissolved H₂ reduces flake formation of steel without adversely affecting the mechanical properties of the alloy.

Thermoelectric Powers of Palladium Alloys

A. T. ALDRED, *J. Phys. Soc. Japan*, 1967, **22**, (3), 762-766

Thermoelectric powers of Pd alloyed with V, Cr, Mn, Fe, Co or Ni are tabulated from data obtained between room temperature and 500°C. In some cases there is a striking composition dependence of thermoelectric power but there is no obvious correlation between thermoelectric power and density of states.

Magnetic Properties of FeRh Alloys in Strong Magnetic Fields

E. A. ZAVADSKII and I. G. FAKIDOV, *Fiz. Tverd. Tela*, 1967, **9**, (1), 139-144

Studies of the magnetisation of 53 at.% Rh-Fe at 77-400°K in magnetic fields up to 330 kOe showed that above the critical temperature T_k, at which the transition from antiferromagnetic to ferromagnetic state takes place, the magnetisation σ (H) reaches saturation. The graph of critical field H_k against temperature is a straight line.

On the Possibility of a Special Triple Point on the P-T Diagram of the Alloy FeRh

E. G. PONYATOVSKII, A. R. KUTSAR and G. T. DUBOVKA, *Kristallografiya*, 1967, **12**, (1), 79-83

Studies on the phase transformation of the equiatomic FeRh alloy by magnetometry and tensometry at 290-700°K, 0-23 kbar showed that the Curie point is depressed but that the transformation temperature is raised in direct proportion to the pressure. The slopes of these lines are -0.6×10^{-3} and 4.7×10^{-3} deg K/bar,

respectively. Extrapolation indicates a triple point at ~ 50 kbar, 630°K . The possibility of a special triple point is considered.

The Rhodium-Selenium System

T. E. RUMMERY and R. D. HEYDING, *Canad. J. Chem.*, 1967, **45**, (2), 131-137

X-ray diffraction and differential thermal analysis revealed eleven phases in the Rh-Se system. β -RhSe_{1.29} and α -RhSe_{1.34} have B 8 structure; RhSe_{2+x} and RhSe_{2.67} have defect pyrite lattices; α -RhSe_{1.95} is isomorphous with IrSe₂. Structures of RhSe_{1±0.13}, β -RhSe_{1.34}, α - and β -RhSe_{1.50} and RhSe_{1.9} remain unknown.

The Crystal Structure of RhHg₂

P. ETTMAYER and B. MATHIS, *Monatsh. Chem.*, 1967, **98**, (2), 505-506

Tetragonal RhHg₂ is isostructural with ξ -PtHg₂, has space group P4/mmm, and unit cell dimensions $a=4.551$, $c=2.998$ Å and $c/a=0.658_8$.

Equiatomic Binary Compounds of Zr with Transition Elements Ru, Rh and Pd

F. E. WANG, *J. Appl. Phys.*, 1967, **38**, (2), 822-824

X-ray studies established an underlying structural similarity among ZrRu, ZrRh and ZrPd and confirmed the existence of an "M₈" transition for ZrRh at 380°C and an "M_f" transition for ZrPd at 550°C . This suggests the existence of unique "martensitic" transition "bands" in the TiNi and ZrPd series of equiatomic binary compounds.

CHEMICAL COMPOUNDS

σ -Complexes of Platinum(II) with Hydrogen, Carbon and Other Elements of Group IV

R. J. CROSS, *Organomet. Chem. Rev.*, 1967, **2**, (1), 97-140

A review of the preparation, structure and properties of organoplatinum (II) complexes, in which H, C, Si, Ge or Sn atoms are σ -bonded to Pt(II). (81 references.)

On the Importance of Platinum Complexes for Coordination Chemistry

A. A. GRINBERG, *Zh. Neorg. Khim.*, 1967, **12**, (4), 842-850

A review of work of the last fifty years, much of it by Grinberg and his associates. (37 references.)

Platinum Complexes Containing Covalent Pt-Au, Pt-Hg and Pt-Sn and Other Metal-to-Metal Bonds

A. J. LAYTON, R. S. NYHOLM, G. A. PNEUMATICAKIS and M. L. TOBE, *Chem. & Ind.*, 1967, (11), 465

Reaction of a transition metal in a low oxidation state with the simple or complex halide of a post-transition metal results in the formation of a metal-metal bond, e.g. tetrakis(triphenylphosphine)-Pt(O) reacts with triphenylphosphine-

aurouschloride to give $(\text{Ph}_3\text{P})_2\text{Cl Pt-Au} \leftarrow \text{PPh}_3$. Pt-Hg, Pt-Cu and Pt-Sn bonds have also been formed. Compounds are characterised by elemental analysis and molecular weight measurements, if soluble.

The Molecules Pd₆Cl₁₂ and Pt₆Cl₁₂ in the Gaseous State. A Contribution to the Problem of M₆X₁₂ Groups

H. SCHÄFER, U. WIESE, K. RINKE and K. BRENDL, *Angew. Chem. Internat. Ed. En.*, 1967, **6**, (3), 253-254

A second form of the Pd₆Cl₁₂ molecule has been found, which is polyhedral in shape, and which is transformed to the chain form at 500°C . Pt₆Cl₁₂ behaves similarly. The polyhedra are held together by Cl bridges.

Chlorination of Palladium and the Behaviour of its Chlorides during Heating

YA. I. IVASHENTSEV and R. I. TIMONOVA, *Zh. Neorg. Khim.*, 1967, **12**, (3), 592-595

Pd powder, which starts to react with Cl₂ at 260°C , reacts most vigorously with complete conversion to chloride at $\geq 525^\circ\text{C}$. O₂ added to Cl₂ prevents sublimation of PdCl₂. Pd only reacts with HCl in the presence of O₂. PdCl₂ decomposes in HCl at 800°C to the metal. PdCl₂ is converted in a stream of O₂ to PdO and to Pd at 780 and 920°C respectively. The endothermic effect at 410°C for PdCl₂ in the O₂ stream is probably related to a change in the crystal lattice.

Hydrolysis of Complex Halides of Palladium

V. I. KAZAKOVA and B. V. PTITSYN, *Ibid.*, 620-625

Hydrolysis constants for K₂[PdCl₄] and K₂[PdBr₄] have approximate values 5.10^5 and $1.7.10^5$. Absorption maxima occur in the ultraviolet at $\lambda_1=226$, $\lambda_2=278$ nm, $\epsilon_1=22.7.10^4$, $\epsilon_2=8.25.10^3$. When alkali is added to K₂[PdCl₄] a colloidal solution of Pd(OH)_x is formed.

Acetylene Complexes of Iridium and Rhodium

J. P. COLLMAN and J. WIKANS, *J. Am. Chem. Soc.*, 1967, **89**, (4), 844-851

Provisional structures of a series of 1:1 molecular acetylene complexes of Ir(I) and Rh(I), illustrating all previously reported complexes of this type, were determined from IR and NMR measurements.

Rhodium and Iridium Porphyrins

E. FLEISCHER and N. SADASIVAN, *Abs. Papers, 153rd Meeting, Am. Chem. Soc.*, 1967, (Apr.), L78

Synthesis of Rh and Ir porphyrins from Rh(I) and Ir(I) carbonyl chlorides, and their characterisation are described. The stable compounds are Rh(III)-porphyrin and Ir(III)CO-porphyrin. The chemistry of these complexes is discussed.

ELECTROCHEMISTRY

Electrodeposited Pt and Pt-Pb Black Electrocatalysts

H. A. ROTH and W. R. LASKO, *Abs. Papers, 153rd Meeting, Am. Chem. Soc.*, 1967, (Apr.), 192

The method of formation of catalytic electrodeposits affects their electrochemical activity. Surface areas of Pt and Pt-Pb electrodeposits can be expressed by $\theta = b\beta t(i/t)^m$, where θ = surface area, β = deposit weight, t = deposit time, i = current density, b and m are constants. Pt-Pb nucleates on Pt electrodes similarly to pure Pt except that the number of nuclei deposited from Pt-Pb solutions is more than from solutions of Pt alone. Microstructure of a deposit affects its physical properties. Electrodeposits of Pt with low i and of Pt-Pb with high i have the greatest surface areas. Amount of Pb discharged is expressed by $\% \text{ Pb} = bt(i/t)^m$.

Recrystallisation of Supported Platinum

J. F. CONNOLLY, R. J. FLANNERY and B. L. MEYERS, *J. Electrochem. Soc.*, 1967, **114**, (3), 241-243

Electrochemical and X-ray diffraction measurements show that loss of 5-90% of the initial area of Pt/C in conducting solutions is not due to poisoning, permanent dissolution of Pt, or temperature effects, but to "electrorecrystallisation" in which Pt is transported as a soluble complex from small to large crystallites by the formation of local cells.

Adsorption and Electrooxidation of Methane on Electrodes of the Platinum Metals

R. V. MARVET and O. A. PETRII, *Elektrokhimiya*, 1967, **3**, (2), 153-161

Reaction potentials for $\text{H}_{\text{ads}} \rightleftharpoons \text{H}^+ + e^-$ were determined in acidic solutions of CH_4 on Pt electrodes during dehydrogenation of CH_4 and reaction of the organic products with H_2 or products of electrooxidation. Low rates of electrooxidation of CH_4 on Pt metals and Ru-Pt alloy electrodes in H_2SO_4 were investigated.

Investigations of the Adsorption of Hydrogen and Oxygen on Dispersed Platinum and Rhodium

M. R. TARASEVICH, K. A. RADYUSHKINA and R. KH. BURSHEIN, *Ibid.*, (4), 455-459

Adsorption studies with H_2 and O_2 of the specific surface areas of Pt and Rh powders showed that adsorption approaches completeness when the potential approaches zero.

Acceleration by Adsorbed Sulphur and Selenium of the Electrochemical Oxidation of Formic Acid on Platinum Catalysts

H. BINDER, A. KÖHLING and G. SANDSTEDE, *Nature*, 1967, **214**, (5085, Apr. 15), 268-269

Activation energy for anodic oxidation of HCOOH

on Raney Pt was decreased considerably by partially covering the 20-40 m^2/g Pt surface with Se or S deposited from SeO in dilute H_2SO_4 or from hot H_2SO_4 respectively.

Degradation Mechanisms of Platinum- and Rhodium-coated Titanium Anodes in the Electrolysis of Chloride and Chloride-Chlorate Solutions

M. ANTLER and C. A. BUTLER, *Electrochem. Technol.*, 1967, **5**, (3-4), 126-130

Tests on Pt/Ti and Rh/Ti anodes for electrolysis of chloride and chloride-chlorate solutions at high current densities revealed dark corrosion films on cut edges, unplated backs of anodes, and spreading from pores in the plates. Corrosion of Ti leads to spalling of plate and loss of precious metal.

Mechanism of the Formation and Reduction of the Oxygen Layer on Iridium in Sulphuric Acid Solution

M. W. BREITER, *Z. Phys. Chem. (Frankfurt)*, 1967, **52**, (1-4), 73-88

The formation and reduction of the O_2 layer adsorbed on Ir wire electrodes was studied voltammetrically with a superimposed a.c. at 30°C, 30 mV/sec. Hysteresis curves of capacity, C_p , against potential indicate that formation and reduction are nearly reversible. Comparison of theoretical and experimental results indicates that OH radicals are formed initially and are subsequently oxidised to O atoms.

ELECTRODEPOSITION AND SURFACE COATINGS

The Electrodeposition of Platinum-Iridium Alloys

C. J. TYRRELL, *Trans. Inst. Met. Finish.*, 1967, **45**, (2), 53-57

Investigations of bright, adherent 70% Pt-Ir alloy coatings deposited from an aqueous electrolyte containing complex bromides of the metals on to etched Ti, sand blasted Ni or Au-flashed Cu, show that consistent deposits are obtained with an electrolyte containing $> 5\text{g/l}$ Pt and $< 10\%$ by weight of Ir operated at 70°C, 1.0 A/dm², pH 1.0-2.0. The coating has a hardness of 200-250 DPN. An increase in temperature results in an increase in Ir content of the deposit. Electrolytes containing 30 g/l Pt, operated at higher current densities are found to give satisfactory results at a faster rate.

Durability of Platinised Titanium Anodes in Electroplating

M. A. WARNE and P. C. S. HAYFIELD, *Ibid.*, 83-92

The preparation, coating thickness and composition, overvoltage, limitations and durability

determined by accelerated laboratory testing, and the influence of current wave formations on durability of Pt/Ti auxiliary anodes in electroplating are described. Their use in commercial Au, Rh, Ni, Cu, Sn and Cr plating, availability and cost are discussed.

LABORATORY APPARATUS AND TECHNIQUE

A Magnetic Device for Detecting Phase Changes at Elevated Temperatures

A. GOLDBERG, W. U. DENT and J. H. MILLER, *J. Sci. Instrum.*, 1967, **44**, (3), 200-202

A simple, compact device for study of phase changes at elevated temperatures needs no coolant and/or vacuum because the primary and secondary coils are made of Pt wires wound on machined ceramic insulators. Temperature capability of the device is up to at least 1150°C in air. Results from simultaneous measurements of magnetic and dilatometric changes are given for heating and cooling of maraging steel from ambient temperature to 815°C.

The Admiralty Pattern Dissolved Oxygen Meter

W. G. JAMES and A. H. FISHER, *Chem. & Ind.*, 1967, (7), 272-274

A modified Admiralty pattern dissolved O₂ meter for measuring low concentrations of O₂ in boiler H₂O was developed with a range of 0 to 0.1 ± 0.001 p.p.m. The presence of dissolved O₂ in the cell causes a current to flow between the C anode and the Pt gauze cathode. The difference between this current and that obtained after depolarisation by stirring is αCO₂ content of the samples. Discharge of a capacitor across a pair of Pt electrodes in the cell produces a known quantity of O₂ enabling the apparatus to be calibrated using the solution under test.

Detection of Hydrogen in Air by Means of Alkali Ion Current from Hot Palladium

S. A. HOENIG, C. W. CARLSON and J. ABRAMOWITZ, *Rev. Sci. Instrum.*, 1967, **38**, (1), 92-94

A surface ionisation detector for H₂ consists of three 0.025 cm diam. Pd wires, each 2 cm long, connected in parallel and heated by a.c. This detector is more sensitive than combustion types and can detect H₂ in air at 1 atm at H₂:air levels as low as 0.1% by volume. It is not sensitive to other atmospheric gases such as O₂, N₂ and CO₂.

HETEROGENEOUS CATALYSIS

Removal of Nitrous Gas Emission by Catalytic Reduction

O. JEITNER and K. KÖNIG, *Chem. Tech.*, 1967, **19**, (3), 166-169

Nitrogen oxides are removed from the tail gas

of the Piesteritz HNO₃ works by reduction of O₂ and the oxides with waste H₂ over 0.5% Pd/Al₂O₃. PH₃ and H₂S, which are catalyst poisons, are removed from the H₂ stream by successive HNO₃ and NaOH washes. A surplus of H₂ of 0.4-0.6% is maintained to ensure complete reduction of the nitrogen oxides. Some NH₃ may form. Recovered N₂ is used as a purge gas.

Test Results from the Oxidation of Ammonia-Air Mixtures on Platinum-Rhenium Gauzes

W. PORZEL, *Ibid.*, 169-171

Re is a suitable alloying element with Pt in gauzes for HNO₃ plants where a yield of 97 to 98% nitrogen oxides from NH₃ is essential. Tests were carried out on 5% Rh-Pt gauzes with replacement of Rh by Re from 0 to 5%. Precious metal losses were similar. Endurance tests on these gauzes were also carried out.

Studies on the Explanation of Processes Occurring in the Capture of Platinum with Calcium Oxide in Nitric Acid Plants

H. SIKORA and E. BLASIAK, *Przemysl Chem.*, 1967, **46**, (3), 141-142

X-ray and chemical studies showed that Pt lost from gauzes in HNO₃ plants is captured by the reaction of PtO₂ with CaO or MgO. ZnO and CaSO₄ are less effective. BaO and CdO form volatile nitrites and nitrates.

Noble Metal Hydroxides on Carbon Non-pyrophoric Dry Catalysts

W. M. PEARLMAN, *Tetrahedron Letters*, 1967, (17), 1663-1664

The preparation and uses of three dry, non-pyrophoric catalysts Pd(OH)₂/C, Rh(OH)₃+Pd(OH)₂/C and Ru(OH)₃+Pd(OH)₂/C are described. Reduction of the metal hydroxide with H₂ yields the active catalysts. Organic solvents may be used safely with the above catalysts. Metal contents are 20% Pd, 10% Rh+0.1% Pd and 10% Ru+0.1% Pd respectively.

Aromatisation of Kerosine Fractions Containing Bicyclonaphthenes. Part 1. Thermodynamic Considerations. Part 2. Conversion of Decalin and Tetralin over a Platinum Reforming Catalyst

M. I. ALLAM and J. C. VLUGTER, *J. Inst. Petrol.*, 1966, **52**, (516), 385-390; 1967, **53**, (517), 44-56

The thermodynamic equilibrium of the model system decalin-tetralin-naphthalene was studied between 0-100 atm and 410-450°C in relation to the conversion of bicyclonaphthenes to more stable aromatics before hydrodealkylation using the Pt reforming catalyst CK-303. The effects of total pressure, p_{H₂}, temperature, contact time and catalyst lifetime on the base materials decalin and tetralin indicate that the dehydrogenation is fast, that naphthalene is strongly adsorbed on

the catalyst and that the carbonaceous deposits from indenes are due to the decalin fraction.

Dehydrogenation of Dicyclohexyl over a Platinum on Alumina Catalyst in the Absence of Added Hydrogen

A. C. NIXON and A. W. RITCHIE, *Abs. Papers, 153rd Meeting, Am. Chem. Soc.*, 1967, (Apr.), Q66

Dehydrogenation of dicyclohexyl in stages to phenylcyclohexane and then to diphenyl is endothermic to the extent of ~1100 Btu, which makes it a possible cooling mechanism for hypersonic aircraft structures. Effects of pressure, temperature and space velocity were studied over Pt/Al₂O₃ at 10–30 atm, 700–1200°F, 30–100 LHSV. Increasing space velocity or pressure increases selectivity for phenylcyclohexane; increasing temperature or dicyclohexyl conversion increases it for diphenyl. Apparent activation energy for dicyclohexane dehydrogenation is 7–8 kcal. More heat sink is available than with methylcyclohexane, provided conversion and temperatures are high and dicyclohexane is thermally more reactive than methylcyclohexane.

On the Production of Hydrogenation Catalysts by the Reduction of Pt(IV) by Means of Electron Donor Solutions

H. HOPFF, *Chimia*, 1967, 21, (2), 87–89

Active hydrogenation catalysts are obtained by impregnating Al₂O₃ or SiO₂ with a solution of PtCl₄ in an electron donor solvent, i.e. CH₃OH, CH₃CO₂C₂H₅, propylene oxide, evaporating off the excess solvent and reducing the Pt(IV) by heating in vacuo for 1 h at 150–200°C.

Effect of Temperature and Ratio of Components on the Kinetics of Hydrogenation of Cyclohexene on Adsorption Platinum Catalysts

L. E. MARTYSHKINA, ZH. V. STREL'NIKOVA and V. P. LEBEDEV, *Vest. Moskov. Univ., Ser. II, Khim.*, 1967, (1), 18–22

The rate of hydrogenation of cyclohexene on 1% Pt/SiO₂ was investigated as a function of p_{H₂} and the reverse and secondary reaction effects were considered. Results indicated that the rate of hydrogenation with excess H₂ or at low temperature could be fitted to a second order rate equation. Decreased p_{H₂} or increased temperature increased the order of the reaction.

Dehydrogenation of Isopropyl Alcohol and Hydrogenolysis of Cyclopentane on Platinum Silica Gel

A. N. MITROFANOVA, V. S. BORONIN and O. M. POLTORAK, *Ibid.*, 95–97

Specific activities of various Pt/SiO₂ catalysts with ~10–30 Å Pt particles were determined as a function of initial rates of dehydrogenation of iso-C₃H₇OH at 160°C, p₀=28 mm Hg, and of

hydrogenolysis of cyclopentane at 298°C, p₀=57 mm Hg. Kinetic curves for the reactions as a function of particle size are given. Results show that activity is unrelated to Pt particle size but agrees with the doublet mechanism of catalysis.

Isomerisation of N-Butane on Platinum-Silica-Alumina Catalysts. I. Isomerisation of Butenes on Silica-Alumina. II. Study of the Reaction of a 0.60 per cent Platinum Catalyst. III. Study of the Influence of Two Types of Active Centres : Platinum and Acid Centres of Silica-Alumina

J. DUBIEN, L. DE MOURGUES and Y. TRAMBOUZE, *Bull. Soc. Chim. Fr.*, 1967, (1), 108–110, 111–114, 114–117

Kinetic studies of the cracking and isomerisation of n-butane at 475°C on three different types of catalyst indicated a three-stage reaction; (1) dehydrogenation of n-butane, (2) isomerisation of butene to isobutene and (3) hydrogenation of isobutene to isobutane. The reaction rate was found to be dependent on Pt content for Pt/SiO₂-Al₂O₃ catalysts containing <0.55% Pt; for catalysts containing >0.55% Pt, the reaction rate was governed by the strong acid sites of SiO₂-Al₂O₃. The rate of reaction in the second stage was found to be lowest on 0.60% Pt/SiO₂-Al₂O₃.

Activation of Supported Nickel Oxide by Platinum and Palladium

E. J. NOWAK and R. M. KOROS, *J. Catalysis*, 1967, 7, (1), 50–54

Hydrogenolysis, isomerisation and aromatisation of n-C₇H₁₆ with H₂ were used to characterise the catalytic activity of 0.6 wt.% Ni/η-Al₂O₃ promoted with Pt and Pd. Tests with 0.3 wt.% and 0.01 wt.% Pt/Al₂O₃ and Pd/Al₂O₃ showed that Pt or Pd in atom ratios to Ni of as little as ~5 × 10⁻³ are sufficient to increase conversion several times, apparently due to Pt- or Pd-catalysed H₂ reduction of supported NiO. Mechanisms and the role of surface diffusion during reduction are discussed.

Mechanisms of Hydrogenolysis and of Isomerisation of Hydrocarbons on Metals. III. Hydrogenolysis of cis- and trans-Dimethyl-1,2-cyclobutanes

G. MAIRE and F. G. GAULT, *Bull. Soc. Chim. Fr.*, 1967, (3), 849–899

Quantitative studies of the hydrogenolysis of cis- and trans-1,2-dimethylcyclobutane to n-hexane, methyl-3-pentane and dimethyl-2, 3-butane, on Pt, Pd, Rh and Ni films show that the cis form produces more n-hexane than the trans form indicating that α,β di-adsorption is an important factor in hydrogenolysis. Fusion of the disubstituted 3,4 bond in the trans isomer to give 2,3-dimethylbutane is the predominant reaction on Rh and Ni films which are more specific for

the reaction than Pt and Pd. The kinetics of the reaction on Pt are discussed.

Oxidation of Ethylene over Palladium and Palladium-Gold Alloys

H. R. GERBERICH and W. K. HALL, *Nature*, 1967, **213**, (5081), 1120

CH_3CHO , the proposed intermediate in the partial oxidation of C_2H_4 to acetic anhydride and CH_3COOH , was present as 1–20% of the products over Pd sponge in a differential reactor. Selectivity was almost independent of temperature but increased as p_{O_2} increased. It reached a maximum over 20 at.% Pd-Au but contamination of this alloy by Na and B may invalidate some results. Apparent activation energy on Pd was 20 kcal/mole.

Kinetics of the Catalytic Hydrolysis of Allyl Chloride in the Presence of Group VIII Metals

R. M. FLID and YA. A. TREGER, *Kinetika i Kataliz*, 1967, **8**, (1), 218–221

The specific catalytic activity and activation energy for the hydrolysis of allyl chloride in alkaline solution for a series of catalysts supported on active C decrease in the order $\text{Rh} > \text{Ni} \approx \text{Pd} > \text{Pt}$, which agrees with the yield and ionisation potential. The nature of the effect of dative bonds in activating molecules of allyl chloride, and in forming intermediate π -allyl complexes, is suggested.

New Routes to Isocyanates—the Reaction of Aromatic Nitro, Nitroso, Azo and Azoxy Compounds with Carbon Monoxide

R. P. BENNETT, W. B. HARDY, R. K. MADISON and S. M. DAVIS, *Abs. Papers, 153rd Meeting, Am. Chem. Soc.*, 1967, (Apr.), O 89

One step conversion of aromatic nitro, nitroso, azo and azoxy compounds to isocyanates is possible by treating their solutions with CO over a Lewis acid-noble metal catalyst at $< 200^\circ\text{C}$, pressures as low as 200 atm. Best catalyst system is supported Rh or Pd with FeCl_3 .

HOMOGENEOUS CATALYSIS

Homogeneous Catalysis in the Reactions of Olefinic Substances. V. Hydrogenation of Soybean Oil Methyl Ester with Triphenylphosphine and Triphenylarsine Palladium Catalysts

H. ITATANI and J. C. BAILAR, *J. Am. Oil Chem. Soc.*, 1967, **44**, (2), 147–151

The order of activity of catalysts in the hydrogenation of soybean oil methyl ester and pure olefinic esters was found to be $(\text{Ph}_3\text{P})_2\text{PdCl}_2 + \text{SnCl}_2 \cdot 2\text{H}_2\text{O} > (\text{Ph}_3\text{P})_2\text{PdCl}_2 + \text{GeCl}_2 > (\text{Ph}_3\text{P})_2\text{Pd}(\text{CN})_2 > (\text{Ph}_3\text{As})_2\text{Pd}(\text{CN})_2 \gg (\text{Ph}_3\text{As})_2\text{PdCl}_2$. An increase in the reaction temperature promotes hydrogenation but pressure change between

13.6 and 39.1 atm had no effect on the reaction rate. Addition of N_2 retarded hydrogenation.

VI. Selective Hydrogenation of Methyl Linoleate and Isomerisation of Methyl Oleate by Homogeneous Catalysis with Platinum Complexes Containing Triphenylphosphine, -arsine, or -stibine

J. C. BAILAR and H. ITATANI, *J. Am. Chem. Soc.*, 1967, **89**, (7), 1592–1599

Investigations of the catalytic activity of Pt complexes of the type $(\text{R}_3\text{Q})_2\text{MX}_2$, where R = alkyl or aryl, Q = P, As or Sb, M = Pt, Pd or Ni, and X = halogen or halogenoid, in the presence of Group IV halides show that methyl oleate undergoes isomerisation from the *cis* to the *trans* form, whereas migration of the double bonds in methyl linoleate to form a conjugated system results in hydrogenolysis to a nonene. A reaction mechanism is suggested.

Aliphatic Alcohols Split Si-Si Bond. Reactions Catalysed by Palladium Chloride Form Variety of Silane Products

Chem. Engng. News, 1967, **45**, (12, March 13), 46–47

Vinylpentamethyldisilane splits at the Si-Si bond when reacted with aliphatic alcohols in the presence of 5–10 mole % PdCl_2 at 0°C to form, among others, trimethylethoxysilane, dimethylvinylethoxysilane, dimethylethylethoxysilane and pentamethylethyldisilane. No cleavage occurs without PdCl_2 . Kyoto University chemists have proposed a model for this reaction which offers a route from olefins to the corresponding aliphatic compounds, and to compounds hard to synthesise, e.g. chloromethyl dimethylisopropylsilane.

Vinyl Acetate via Ethylene

Chem. Process Engng., 1967, **48**, (3), 71–72, 78
Patent literature for the oxidation of ethylene to vinyl acetate is reviewed and a flow sheet for a one-step oxidation using a PdCl_2 catalyst with CuCl_2 as oxidising agent at 120–130°C and 150 psig is suggested with a 19% return on capital.

Hoechst-Bayer Route to VA Cuts Raw Material Costs

Eur. Chem. News., 1967, **11**, (272, April 14), 40, 42

This new process using 0.1–2.0 wt.% Pd/ Al_2O_3 or Pd/ SiO_2 is compared with the Hoechst-Wacker process using PdCl_2 - CuCl_2 as catalyst.

The Oxidative Coupling of Vinyl Acetate with Palladium Acetate; Synthesis of 1,4-Diacetoxy-1,3-butadiene

C. F. KOHLL and R. VAN HELDEN, *Rec. Trav. Chim.*, 1967, **86**, (3), 193–200

Oxidative coupling of vinyl acetate with $\text{Pd}(\text{OAc})_2$ occurs at 60°C to give 1,4-diacetoxy-1,3-butadiene in *trans*, *trans* configuration, 1,1,4-triacetoxy-2-

butene and 1,1,4,4-tetraacetoxybutane, with reduction of Pd(OAc)₂ to Pd metal.

Organic Syntheses by Means of Noble Metal Compounds. XXVIII. Synthesis of a New Type of π -Allylic Palladium Complexes from α,β - and β,γ -Unsaturated Esters and Their Carbonylation

J. TSUJI and S. IMAMURA, *Bull. Chem. Soc. Japan*, 1967, **40**, (1), 197-201

PdCl₂ reacts with α,β - and β,γ -unsaturated carbonyl compounds, i.e. those with an active H in an allylic position, to form dimeric π -allylic complexes, the NMR spectra of which are discussed. Carbonylation of the π -allylic complexes to yield a higher β,γ -unsaturated ester suggest a synthetic method by the stepwise introduction of CO.

The Dimerisation of Alkenes by Palladium and Rhodium Chlorides

A. D. KETLEY, L. P. FISHER, A. J. BERLIN, C. R. MORGAN, E. H. GORMAN and T. R. STEADMAN, *Inorg. Chem.*, 1967, **6**, (4), 657-663

Studies of the dimerisation of C₂H₄ and C₃H₆ at 10 atm, 50°C show that the reaction is catalysed by PdCl₂ and various organic solvents, which also catalyse isomerisation of the olefin-PdCl₂ π -complexes. On standing for several days the latter are converted to inactive π -allyl complexes. RhCl₃ with the solvents gives similar results but the mechanism is believed to be different.

Homogeneous Catalytic Hydrogenation of Unsaturated Aldehydes to Form Saturated Aldehydes

F. H. JARDINE and G. WILKINSON, *J. Chem. Soc., C, Org.*, 1967, (4), 270-271

Dissociation of tris(triphenylphosphine)chlororhodium in C₆H₆ in the presence of molecular H₂ yields an effective catalyst for selective hydrogenation of acetylenic and ethylenic bonds at 25°C and atm. pressure, e.g. propenal, but-2-enal and *trans*-2-methylpent-2-enal to the corresponding saturated aldehydes. The side reaction of decarbonylation is minimised by the use of dilute solutions in benzene but this makes the recovery of the product more difficult.

Syntheses with Carbon Monoxide. X. Hydroformylation of Unsaturated Carboxylic Acid Esters with Rhodium Catalysts

J. FALBE and N. HUPPES, *Brennstoff-Chem.*, 1967, **48**, (2), 46-52

α,β -Unsaturated carboxylic acids, which are unaffected in reactions with Co catalysts, can be hydroformylated with good yields using Rh₂O₃ as catalyst. Products vary according to reaction conditions, e.g. methyl acrylate is converted to α -isobutyl formate, β -isobutyl formate or α -methyl- γ -butyrolactone; cinnamic acid ester is converted to β -phenyl- γ -butyrolactone.

Olefin Coordination Compounds of Rhodium. IV. The Mechanisms of the Synthesis of 1,4-Hexadiene from Ethylene and Butadiene and of its Isomerisation to 2,4-Hexadiene

R. CRAMER, *J. Am. Chem. Soc.*, 1967, **89**, (7), 1633-1639

Selective hexadiene production from C₂H₄-butadiene mixtures occurs by thermodynamic control via relatively stable π -crotylrhodium(III)-C₂H₄ complex. Rh alkyl catalyst is formed in situ by reduction of Rh(III) to Rh(I) followed by protonation and olefin insertion. After its formation the oxidation number of Rh does not alter during hexadiene synthesis. Hexadiene and monoolefin isomerisation are similar but sequestration of the catalyst by product conjugated diene retards the former reaction.

Homogeneous Air Oxidations with Osmium Catalyst

L. STAUTZENBERGER, A. F. MACLEAN and C. C. HOBBS, *Abs. Papers, 153rd Meeting, Am. Chem. Soc.*, 1967, (Apr.), Q54

Air-oxidation of Os(VI) oxide to Os(VIII)O₄ in aqueous solution at pH 8.5-11, (maximum rate at 30°C, pH 9.5), makes in situ regeneration of OsO₄ possible using O₂. Hydroxylation of C₂H₄ to ethylene glycol thereby becomes attractive; it is efficient with C₂H₄ and O₂ consumed in stoichiometric ratio but ethylene glycol inhibits reoxidation of Os(VI). Rate became impractically low at 50°C, 1 atm, 0.5% glycol concentration. Rate increased at high pO₂; at 1000 psi, glycol concentration >5% is reached.

FUEL CELLS

Fuel Cell Performance as a Function of Catalyst Surface Area

H. I. ZELIGER, *J. Electrochem. Soc.*, 1967, **114**, (2), 144-145

Fuel cell performance as a function of specific area of a number of Pt/asbestos electrodes, containing 1-6% Pt, was evaluated by investigating current density produced per unit area of Pt at 0.7V. The tabulated results indicate good correlation between the surface area of Pt and current produced, and support the theory that only the exposed surface area of catalyst is catalytically effective.

CHEMICAL TECHNOLOGY

Pilot Plant Development of an Electrolytic Dissolver for Stainless Steel Alloy Nuclear Fuels

L. T. LAKEY and W. B. KERR, *Ind. Engng. Chem., Process Des. Dev.*, 1967, **6**, (2), 174-179

A thin Pt sheet is used as anode in an electrolytic

dissolver for stainless steel-UO₂ cermet nuclear fuels. The pilot plant uses a Nb fuel basket and Ti for the dissolver shell, which acts also as the cathode. The full-scale plant would use a Nb anode with a thin Pt sheet on its surface. The stainless steel dissolves in the nitric acid electrolyte by being made anodic. Pt losses were only 0.05 mil/month.

TEMPERATURE MEASUREMENT

The Electrical Resistivity of Thermometrically Pure Platinum below 11°K

J. F. KOS and J. L. G. LAMARCHE, *Canad. J. Phys.*, 1967, **45**, (2, pt.1), 339-354

To extend the use of the Pt resistance thermometer as a standard down to 4.2°K, an interpolation of

the resistance versus temperature function of pure Pt was made to $\pm 0.01^\circ\text{K}$ at 4.2-10°K from calibration points above 10°K and below 4.2°K. Experimental results required a new expression to describe them satisfactorily by accounting for conductivity of electrons in the second band.

Holding at $\pm 0.04^\circ\text{F}$

C. J. CHASSE and R. Y. RUSLING, *Instrumentation*, 1966, **19**, (4), 2-7

The temperature of 17.5 nautical miles of 1 in. diameter undersea cable was maintained at $75^\circ \pm 0.04^\circ\text{F}$ in a water bath for 24 h using ten high grade waterproof thermistors, located at different places in the coiled cable, in conjunction with 2 master thermistors connected to a water proofed platinum resistance thermometer which controlled the temperature of the inflowing water.

NEW PATENTS

METALS AND ALLOYS

Grain-refined Uranium-Aluminium Alloys

U.K. ATOMIC ENERGY AUTHORITY

U.S. Patent 3,285,737

Suitable grain refining agents, for alloys of U with 100-1,500 p.p.m. Al, include Rh, Ir, Os, Ru, Pt, etc.

Tungsten-Ruthenium Alloy

P. R. MALLORY & CO. INC. *U.S. Patent* 3,301,641

An easily worked ductile alloy contains 90% W, 6% Ni, 2% Mo, 1.5% Fe and 0.5% Ru. It may be produced by powder metallurgy.

Spinnerette Alloy

JOHNSON, MATTHEY & CO. LTD.

Belgian Patent 684,532 *Dutch Appl.* 66.10,352

Spinnerettes with uniform alloy structure, resistance to corrosion and small grain size consist of 50-80% Au-0.04-0.5% Ir-Pt, preferably 70% Au-29.8% Pt-0.2% Ir, which is made by induction-melting the constituents, followed by homogenisation by heat treatment.

Platinum-clad Refractory Metal

JOHNSON, MATTHEY & CO. LTD.

Belgian Patent 686,000

Pt group metal is bonded to a refractory metal by using an intermediate barrier layer composed of a mixture of a refractory ceramic material and a metal which is insoluble in one of the metals to be joined but is soluble in the other. In particular, Pt layer on Mo is bonded using Au com-

bined with Al₂O₃, on Nb using Au with Al₂O₃, ZrO₂ or ThO₂.

ELECTROCHEMISTRY

Method and Apparatus for Performing Electrolytic Processes

ALBRIGHT & WILSON LTD. *British Patent* 1,056,889

Electrolytic cells have cathodes of Pt/Ti and anodes of a metal resistant to nascent H, e.g. Cu.

Hydrogen Oxidation in Cells

THE U.S. NATIONAL AERONAUTICS AND SPACE ADMINISTRATION *U.S. Patent* 3,287,174

Pressure build-up in electrochemical cells is prevented by introducing PdO to convert H₂ to H₂O.

Alkali-Chlorine Cell Anode

PITTSBURGH PLATE GLASS CO.

U.S. Patent 3,287,250

The anode has a Pt surface activated by prior exposure as a cathode in an electrolyte inert to Pt.

Noble Metal-coated Valve Metal Electrodes

IONICS INC.

U.S. Patent 3,291,716

Electrodialysis equipment uses Pt/Ta electrodes.

Activation of Metal Surfaces

JOHNSON, MATTHEY & CO. LTD.

German Patent 1,236,302

Surfaces of Pt group metals and their alloys, especially in the form of electrolysis electrodes,