

# ABSTRACTS

## of current literature on the platinum metals and their alloys

### PROPERTIES

#### An Investigation of the Palladium-Gold-Nickel Alloy System

A. T. GRIGOR'EV, L. A. PANTELEIMONOV, V. V. KUPRINA, G. V. GOLDOBINA and M. A. RUDNITSKII, *Zhur. Neorg. Khim.*, 1962, 7, (5), 1110-1116

Alloys with Pd content fixed at 10, 20, 30, 40, 50, 60, 70, 80, or 90 wt.% and variable amounts of Au and Ni were studied by thermal analysis and determination of hardness, microstructure, specific electrical resistance and its temperature coefficient. It was shown that a continuous series of solid solutions is formed immediately after solidification. Alloys with up to 20 wt.% Pd undergo decomposition in the solid state with the formation of a wide region of mechanical mixtures. Curves showing the relationship between composition and physical properties are given.

#### The Constitution Diagram of the Osmium-Ruthenium Alloy System

M. A. TYLKINA, V. P. POLYAKOVA and E. M. SAVITSKII, *Zhur. Neorg. Khim.*, 1962, 7, (6), 1467-1468

The diagram was constructed by methods of physico-chemical analysis. Alloy samples in both the cast and annealed state were examined. A continuous series of solid solutions with melting temperatures between those of Os (3050°C) and Ru (2250°C) was found. Cast alloys at all compositions showed a dendritic structure. The hardness is variable with a maximum in the composition range 60-70 wt.% Os.

#### The Constitution Diagram of the Osmium-Rhenium System

M. A. TYLKINA, V. P. POLYAKOVA and E. M. SAVITSKII, *Zhur. Neorg. Khim.*, 1962, 7, (6), 1469-1470

Physico-chemical methods were used to examine alloys of the system. An uninterrupted series of solid solutions with melting temperatures between those of Os (3050°C) and Re (3170°C) was found. Maximum hardness for alloys in the cast and annealed states is obtained in the composition range 60-70 at.% Os.

#### An Investigation of Alloys of Bismuth with Platinum in the Range 10 to 50 At.% Platinum

N. N. ZHURAVLEV, G. S. ZHDANOV and E. M. SMIRNOVA, *Fiz. Metallov i Metalloved.*, 1962, 13, (4), 536-545

The portion of the Pt-Bi phase diagram which lies between the compounds PtBi and PtBi<sub>2</sub> was

determined precisely by thermal analysis and X-ray and metallographic phase analysis. A  $\gamma$ -phase (? Pt<sub>2</sub>Bi<sub>3</sub>) formed by a peritectic reaction exists between PtBi and PtBi<sub>2</sub> and undergoes eutectoid decomposition into PtBi and PtBi<sub>2</sub>. Superconductivity of the alloys was studied.

#### The Constitution Diagram of the Palladium-Iridium System

M. A. TYLKINA, V. P. POLYAKOVA and E. M. SAVITSKII, *Zhur. Neorg. Khim.*, 1962, 7, (6), 1471-1473

The system was investigated by thermal analysis, microstructural and X-ray phase analysis, and by hardness measurements. A peritectic-type diagram with two limited solid solutions ( $\alpha$ -solid solution of Ir in Pd and  $\beta$ -solid solution of Pd in Ir) was constructed. A two-phase ( $\alpha + \beta$ ) region exists between the  $\alpha$ - and  $\beta$ -solid solutions. No chemical compounds were detected in the system. Hardness measurements confirmed the microstructural and thermal analysis of the system.

#### Borides of Ruthenium, Osmium and Iridium

B. ARONSSON, E. STENBERG and J. ÅSELIUS, *Nature*, 1962, 195, (Jul. 28), 378-379

Crystallographic constants are given for the phases Ru<sub>7</sub>B<sub>3</sub>, Ru<sub>11</sub>B<sub>8</sub>, RuB $\sim$ <sub>1.13</sub>, RuB $\sim$ <sub>1.65</sub>, RuB $\sim$ <sub>2.15</sub>, OsB $\sim$ <sub>1.25</sub>, OsB $\sim$ <sub>1.65</sub>, OsB $\sim$ <sub>2.25</sub>, IrB $\sim$ <sub>1.15</sub> and IrB $\sim$ <sub>1.5</sub>.

#### Conductivity and Hall Constant. XXIII. The Temperature Dependence of Resistance and Hall Constant of Palladium Alloys

W. GMÖHLING and D. HAGMANN, *Z. Metallkunde*, 1962, 53, (7), 459-465

Measurements of the temperature coefficient of resistivity and Hall coefficient at room temperature were made on alloys of Pd with up to 4 at.% Ag, Cd, In, Rh, Ru, Mo, Nb, Zr, or V. It was found that the absolute temperature coefficient of resistivity is decreased by all alloying additions. An even more marked decrease in the absolute temperature coefficient of the Hall constant occurs on addition of the alloying metals. These changes are related to changes in the electronic structure of the Pd.

#### Thermodynamics of Ordering Alloys. IV. Heats of Formation of Some Alloys of Transition Metals

R. ORIANI and W. K. MURPHY, *Acta Met.*, 1962, 10, (9), 879-885

The heats of formation of Ag-Pd, Cu-Pd, Cu-Pt and Co-Pt alloys were measured at 642°, 642°

640°, and 641°C, respectively, and at temperatures in the range 500°-740°C for the alloy Cu<sub>0.6</sub>Pd<sub>0.4</sub>. Large negative enthalpies of formation were found for these alloys and large negative excess entropies of formation were calculated.

#### **Electrical Resistivity Recovery in Cold-worked 60% Silver-40% Palladium Alloy**

K. K. RAO, *Acta Met.*, 1962, **10**, (9), 900

Decreases in resistivity of the plastically deformed alloy were observed between 80-120°C and between 240-300°C. The specimen was held at various temperatures in these ranges for 30 min. periods.

#### **A Contribution on the Structure of the Palladium-Ruthenium System and on the Properties of Palladium-Rich Alloys**

W. OBROWSKI and G. ZWINGMANN, *Z. Metallkunde*, 1962, **53**, (7), 543-455

The structure of alloys containing up to 40 at.% Ru was investigated by thermal, X-ray and microscopic methods. Measurements of hardness, specific electrical resistance and its temperature coefficient, thermoelectric properties and lattice constants were made and corrosion properties were observed. No evidence of a stable intermetallic phase was found. The possibility of age-hardening alloys with 6 to 10 at.% Ru was shown. Corrosion properties were found to be similar to those of pure Pd. Internal oxidation occurs on heating the alloys in an oxygen-containing atmosphere.

#### **Stability of Solid Phases in the Ternary Systems of Silicon and Carbon with Rhenium and the Six Platinum Metals**

A. W. SEARCY and L. N. FINNIE, *J. Amer. Ceram. Soc.*, 1962, **45**, (6), 268-273

Phase studies were carried out at 1600°C for Re-Si-C, 1340°C for Ru-Si-C and Ir-Si-C, 1350°C for Os-Si-C, and 1170°C for Rh-Si-C. The only stable phases at these temperatures are solid metal silicides and SiC. The Pt-Si-C and Pd-Si-C systems were examined during cooling from above the liquidus temperatures. The thermodynamic stabilities of the metal silicides was studied, and heats of formation for the Pt metal silicides were estimated.

#### **An Anomaly in the Electrical Resistance and Formation of the K-State in the Palladium-Tungsten and Palladium-Molybdenum Systems**

V. S. MES'KIN, R. I. SERGIENKO and L. A. POPOVA, *Fiz. Metallov i Metalloved.*, 1962, **13**, (1), 126-131  
Pd alloys containing 13-20 wt.% W and 5.5-10% Mo show anomalous electrical resistance on annealing. The production of the K-state in these alloys is indicated. Variations in the electrical properties of these alloys on the formation of the K-state were investigated.

#### **Activities of Iron in Iron-Platinum Alloys at 1300°C**

R. W. TAYLOR and A. MUAN, *Trans. Met. Soc. A.I.M.E.*, 1962, **224**, (3), 500-502

Mixtures of Pt metal and Fe<sub>2</sub>O<sub>3</sub> were equilibrated at 1300°C and at known oxygen pressures. Compositions of Fe-Pt alloy phases at equilibrium were determined by measurement of weight changes of the mixtures and are shown graphically with those of the Fe oxide phase. A negative deviation from Raoult's law is shown by the activity of Fe in Fe-Pt alloys.

#### **The Electrical Resistivities of the Palladium-Silver Alloys**

B. R. COLES and J. C. TAYLOR, *Proc. Roy. Soc., Series A*, 1962, **267**, (1328), 139-145

Resistance measurements were made on wire specimens of alloys of the system and resistivities were calculated as a function of temperature and composition. Residual resistivity and temperature-dependent resistivity were calculated using the theoretical model of Mott and the observed values for the density of electron states at the Fermi surface. With the exception of the temperature-dependent resistivity near pure Pd, good agreement was obtained between experimental and theoretical results.

#### **Alloys of the First Transition Series with Palladium and Platinum**

S. J. PICKART and R. NATHANS, *J. Appl. Phys., Suppl.* to 1962, **33**, (3), 1336-1338

Neutron diffraction measurements were used to determine the magnetic moments on the constituent atoms of the ordered alloys FePd<sub>3</sub>, MnPt<sub>3</sub>, and Cr<sub>0.3</sub>Pt<sub>0.7</sub>. The results for FePd<sub>3</sub> are consistent with those obtained by other workers from magnetisation measurements. At room temperature the magnetic ordering in Cr<sub>0.3</sub>Pt<sub>0.7</sub> is ferrimagnetic.

#### **Neutron Diffraction Investigations of Ferromagnetic Palladium and Iron Group Alloys**

J. W. CABLE, E. O. WOLLAN, W. C. KOEHLER and M. K. WILKINSON, *J. Appl. Phys., Suppl.* to 1962, **33**, (3), 1340

The individual magnetic moments of the constituent atoms of the ferromagnetic alloys Pd<sub>3</sub>Fe, PdFe, Pd<sub>3</sub>Co, PdCo, Ni<sub>3</sub>Co, and NiCo were determined by the combination of neutron diffraction and magnetic induction measurements. Results are given in a table.

#### **Anomalous Magnetic Moments and Transformations in the Ordered Alloy FeRh**

J. S. KOUVEL and C. C. HARTELIUS, *J. Appl. Phys., Suppl.* to 1962, **33**, (3), 1343-1344

Magnetisation and electrical resistivity measurements were made on an Fe-Rh alloy containing 52 at.% Rh. A first-order antiferromagnetic-ferromagnetic transition at about 350°K indicated

by earlier X-ray and neutron diffraction investigations was confirmed. The alloy has a ferromagnetic Curie temperature of 675°K.

### Platinum Group Metals and Rhenium

A. V. FRANCIS, *Métallurgie*, 1962, **94**, (3), 233-245

The chemical, physical, and mechanical properties of the Pt metals and their alloys are described. Industrial applications of the Pt metals are discussed. The production of Re and its applications, together with those of its alloys with Mo and Ir, are outlined.

### Contact Potential in Thin Metal Films

S. M. BRYLA and C. FELDMAN, *J. Appl. Phys.*, 1962, **33**, (3), 774-776

Contact potential difference between a Pt reference surface and films of Au, Pt, and Ag was measured in an attempt to find a work function variation with film thickness. The films were vacuum deposited on to fused SiO<sub>2</sub> substrates. In the range of 5 ohms/sq. to 10<sup>8</sup> ohms/sq. the contact potential was found to be independent of film resistance or thickness.

### Temperature Coefficient of Electrical Resistance of High-Purity Rhodium

E. G. PRICE and B. TAYLOR, *Nature*, 1962, **195**, (Jul. 21), 272-273

Resistivity measurements were made on commercial grade and specially purified Rh wire. The temperature coefficient of electrical resistance between 0° and 100°C for the commercial grade Rh was found to be 0.00461 and that for purified Rh was 0.00463. Mass-spectrographic analyses of both samples are given.

J. C. CHASTON, *Nature*, 1962, **195**, (Aug. 25), 793

Measurements made in 1936 on specially purified Rh gave a value of 0.00463 for the temperature coefficient of electrical resistance.

### Structure of Hydrides of Palladium

J. G. ASTON and P. MITACEK, *Nature*, 1962, **195**, (Jul. 7), 70-71

Heat capacities of PdH<sub>x</sub> for x = 0.5 and x = 0.75 were determined, and it is shown that between 35°K and 85°K the heat capacity is independent of hydrogen concentration up to 0.75 H/Pd ratio. Structures are proposed for the β-phase and α-phase hydrides. Ring diffusion and long-range diffusion processes cause the warm drifts observed between 150°K and 200°K and between 200°K and 250°K, respectively.

### The Vapour Pressure of Palladium

R. F. HAMPSON and R. F. WALKER, *J. Res. Nat. Bur. Stds., Section A*, 1962, **66A**, (2), 177-178

A vacuum microbalance technique was used in the measurement of vapour pressure and heat of sublimation. Over the temperature range 1294° to 1488°K the measured vapour pressures may be

represented by  $\log P_{\text{mm}} = 8.749 - 18655/T$ . The mean heat of sublimation obtained was  $89.2 \pm 0.2$  kcal/mole. The normal boiling point is estimated to be 3200°K.

### Electrochemical Determination of the Heat of Adsorption of Hydrogen on Finely Divided Palladium

ZH. L. VERT, I. A. MOSEVICH and I. R. TVERDOVSKII, *Proc. Acad. Sci. U.S.S.R., Phys. Chem. Section*, 1961, **140**, (1-6), 662-664 (Transl. of *Doklady Akad. Nauk S.S.S.R.*, 1961, **140**, (1), 149-152)

It was shown by the study of charge curves that in the presence of SO<sub>4</sub><sup>2-</sup> ions the heats of adsorption, Q, remain constant at 27.5 kcal/mole in the range  $0 < \theta < 0.5$  ( $\theta$  = fraction of surface covered by hydrogen). As  $\theta$  increases above 0.5, Q decreases. The heat of adsorption of hydrogen found in HCl solutions is lower than the value found in H<sub>2</sub>SO<sub>4</sub> solutions. The heats of adsorption on several Pd-Ag alloys were determined in 1N H<sub>2</sub>SO<sub>4</sub>.

### Electrical Resistance of Alpha Hydrogen-Palladium

W. T. LINDSAY and F. W. PEMENT, *J. Chem. Phys.*, 1962, **36**, (5), 1229-1234

Resistance measurements were made on gas-charged αH-Pd wires, 0.1 mm in diameter, in the temperature range 100-400°C. It was found that the small increase of Pd resistance on adding hydrogen is proportional to hydrogen concentration and that the constant of proportionality is independent of temperature. In the range 75-400°C and for α-phase compositions up to 0.1 m, the observed data may be expressed by the equation:  $(R_{\text{Pd}}/R_{\text{Pd}}^0) - 1 = (2.41 \pm 0.04) m$ , where R = resistance of αH-Pd, R<sup>0</sup> = resistance of hydrogen-free Pd, and m = H:Pd atom ratio.

### Interaction of Helium, Neon, Argon, and Krypton with a Clean Platinum Surface

H. CHON, R. A. FISHER, R. D. MCCAMMON and J. G. ASTON, *J. Chem. Phys.*, 1962, **36**, (5), 1378-1382

Heats of adsorption of He, Ne, Ar, and Kr on Pt were measured and the values obtained were compared with those calculated theoretically for the attractive part of interaction energy between a nonpolar gas and a metal surface.

### Study of the Adsorption of Hydrogen, Ethane, Ethylene, and Acetylene on Iridium by Field Emission Microscopy

J. R. ARTHUR and R. S. HANSEN, *J. Chem. Phys.*, 1962, **36**, (8), 2062-2071

Changes in emission patterns and work functions resulting from time- and temperature-dependent surface reactions were studied. In the temperature range 70°-300°K a rather uniform covering of the high index faces of Ir was indicated. Surfaces containing adsorbed species were flashed to various temperatures for various periods of time.

Results showed that hydrogen,  $C_2H_4$ , and  $C_2H_2$  are chemisorbed by Ir below  $77^\circ K$ , and  $C_2H_6$  is largely physically adsorbed. Hydrogen is desorbed over the temperature range  $200^\circ-400^\circ K$ , adsorbed  $C_2H_4$  decomposes at about  $200^\circ K$  to  $C_2H_2$  and hydrogen (both of which are then adsorbed), and adsorbed  $C_2H_2$  dehydrogenates over the temperature range  $400^\circ-600^\circ K$ .

### **Palladium and Palladium Alloys for the Preparation of High-purity Hydrogen**

G. F. P. MÜLLER, *Z. Metallkunde*, 1962, **53**, (7), 449-453

Hydrogen diffusion and solubility in Pd, 20% Au-Pd and 30% Au-Pd were measured. The dependence on temperature of the hydrogen diffusion and the electrical resistance of Pd was investigated during thermal cycling. Changes in the mechanical properties of Pd and Ag-Pd on heating in hydrogen were also studied and correlated with the structure of the PdH formed. The construction of diffusion cells for the purification of hydrogen and for its separation from other gases is discussed.

## **ELECTROCHEMISTRY**

### **Anodic Oxidation of Methanol on Platinum. I. Adsorption of Methanol, Oxygen, and Hydrogen on Platinum in Acidic Solution**

M. W. BREITER and S. GILMAN, *J. Electrochem. Soc.*, 1962, **109**, (7), 622-627

Potentiostatic and galvanostatic techniques were used to determine the coverage of bright Pt electrodes with  $CH_3OH$ , hydrogen, and oxygen in 1N  $HClO_4$  containing different amounts of  $CH_3OH$ .  $CH_3OH$  coverage is independent of potential between +0.1 and +0.6 V and decreases rapidly with potential above +0.6 V during the anodic sweep of the current-potential curve. Saturation coverage of  $CH_3OH$  present on the surface decreases hydrogen adsorption by 75%. Oxygen coverage in 1N  $HClO_4$  and 1N  $HClO_4$  + 1M  $CH_3OH$  is nearly the same.

### **The Utilisation of the Palladium-Hydrogen Electrode**

H. SHIRATORI, *J. Electrochem. Soc. Japan*, 1961, **29**, (3), E-161

A Pd-H alloy in which  $\alpha$ - and  $\beta$ -phases coexist may be used in the measurement of the pH of a solution and as a reference electrode in potential measurement.

## **ELECTRODEPOSITION**

### **Industrial Applications of Noble Metal Plating**

G. BACQUIAS, *Métallurgie*, 1962, **94**, (6), 623-626

The properties of electrodeposited Ag, Au, Rh, Pd, and Pt are compared and criteria by which

suitable coatings may be selected are given. Modern methods for obtaining homogeneous deposits are discussed. Applications in the electrical and electronic industries are mentioned.

## **METAL WORKING**

### **Brazing for Elevated Temperature Service**

D. W. RHYS and W. BETTERIDGE, *Metal Industry*, 1962, **101**, (1), 2-4; (2), 27-30; (3), 45-46

Various brazing methods and the design of joints are described. Brazing conditions and requirements for many individual basis materials and the suitability of particular brazing alloys are discussed. The properties of the most common brazing alloys are described and the applications of brazed joints using these materials are considered. Pd-containing brazing alloys are recommended for many high-temperature applications.

## **CATALYSIS**

### **Competitive Catalytic Hydrogenation of Benzene, Toluene and the Polymethylbenzenes on Platinum**

C. P. RADER and H. A. SMITH, *J. Amer. Chem. Soc.*, 1962, **84**, (8), 1443-1449

Adams' ( $PtO_2$ ) catalyst was used in the hydrogenation reactions which were carried out at  $30^\circ C$  in the hydrogen pressure range 35-60 p.s.i. The relative ease of adsorption of the hydrocarbons on the active catalyst surface does not necessarily correspond to the relative reduction rates of the individual hydrocarbons. With the exception of  $C_6(CH_3)_6$ , ease of adsorption decreases with increasing nuclear substitution and for a given set of polymethylbenzene isomers, decreases with increasing symmetry of substitution. The mechanism of the reduction process is discussed.

### **New, Highly Active Metal Catalysts for the Hydrolysis of Borohydride**

H. C. BROWN and C. A. BROWN, *J. Amer. Chem. Soc.*, 1962, **84**, (8), 1493-1494

The catalytic effect of Ru, Rh, Pd, Os, Ir, and Pt on the hydrolysis of a solution of  $NaBH_4$  was investigated. 5 ml of a 0.100 M solution of the Pt metal salt was injected into a stirred solution of 1 g  $NaBH_4$  in 45 ml  $H_2O$  at  $25^\circ C$ . The Pt metal salts were reduced to the corresponding pure metal powder and hydrogen was evolved. Catalytic activity observed was in the order: Ru, Rh > Pt > Os > Ir > Pd.

### **A Simple Preparation of Highly Active Platinum Metal Catalysts for Catalytic Hydrogenation**

*Ibid.*, 1494-1495

Finely-divided Pt metal catalysts produced *in situ* by  $NaBH_4$  reduction were used in the hydrogenation of 1-octene. With Pt as catalyst,

absorption of hydrogen was complete in 16 to 18 min. On a weight basis, Rh is approximately twice as effective as the Pt catalyst and almost four times as effective as commercial PtO<sub>2</sub> catalyst in this hydrogenation reaction. Ru, Pd, Os, and Ir are less effective than commercial PtO<sub>2</sub>.

#### A New Convenient Technique for the Hydrogenation of Unsaturated Compounds *Ibid.*, 1495

A Pt catalyst formed *in situ* by NaBH<sub>4</sub> reduction of H<sub>2</sub>PtCl<sub>6</sub> and hydrogen generated *in situ* by the hydrolysis of NaBH<sub>4</sub> were used in the laboratory-scale hydrogenation of unsaturated compounds. 1-Octene, 2-octene, 2, 4, 4-trimethyl-1-pentene, cyclohexene, cyclooctene, norbornene, 4-vinylcyclohexene and 3-hexyne underwent quite rapid hydrogenation. The reaction time for 1-octene is 9-10 min.

#### Stereochemistry and Mechanism of Silane Additions to Olefins. II. Chloroplatinic Acid-Catalysed Addition of Trichlorosilane to Alkylcyclohexenes

T. G. SELIN and R. WEST, *J. Amer. Chem. Soc.*, 1962, **84**, (10), 1863-1868

Addition of HSiCl<sub>3</sub> to 4-methylcyclohexene, 1-methylcyclohexene and 1-ethylcyclohexene in the presence of H<sub>2</sub>PtCl<sub>6</sub> resulted in terminal adducts. With 4, 4-dimethylcyclohexene, addition to the ring was observed. Addition to 4-methylcyclohexene is preceded by isomerisation to 1-methylcyclohexene. HSiCl<sub>3</sub> does not add to 1-*n*-propylcyclohexene and 1-*n*-octylcyclohexene. Mechanisms for the addition reactions are discussed and it is suggested that the addition occurs through a specific olefin-catalyst or olefin-catalyst-silane intermediate.

#### Differences in the Catalytic Activity of Nickel, Platinum and Palladium as Observed in the Isotopic Exchange Reaction of Paraxylene with Deuterium Oxide

K. HIROTA and T. UEDA, *Bull. Chem. Soc. Japan*, 1962, **35**, (2), 228-232

This investigation confirmed that with a Ni catalyst only hydrogen atoms of methyl groups of paraxylene exchange with D<sub>2</sub>O. With Pt black and Pd black catalysts and under similar experimental conditions, hydrogen atoms of both methyl groups and the benzene ring exchange with D<sub>2</sub>O. Ni/Al<sub>2</sub>O<sub>3</sub> has a similar catalytic activity to Pt black and Pd black in this exchange reaction, but with Ni/SiO<sub>2</sub> and Ni/kieselguhr there is no exchange of hydrogen in the benzene ring.

#### Cold Hydrogenation of C<sub>3</sub>-Fractions in the Liquid Phase

W. KRÖNIG, *Erdöl u. Kohle*, 1962, **15**, (3), 176-179  
The liquid phase selective hydrogenation of the

C<sub>3</sub>-fraction in order to remove contaminants from C<sub>3</sub>H<sub>8</sub> may be carried out in the temperature range 10° to 20°C with the use of a Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. The successful operation of this process in the trickle phase on a commercial scale is described. Other applications of cold hydrogenation in refining processes not restricted to C<sub>3</sub>-fractions are described.

#### A New Branch of Petrochemistry - The Technique of Producing Aromatics from Petroleum

G. VOSS, *Erdöl u. Kohle*, 1962, **15**, (5), 387-391

The development is described of the petrochemical industry of West Germany and the U.S.A., with particular reference to the production of aromatic hydrocarbons. Modern methods of producing aromatics from petroleum are described and illustrated by flow diagrams. The use of Pt/Al<sub>2</sub>O<sub>3</sub> catalysts in the Platforming and Octafining processes is mentioned.

#### Catalysts and Chemicals in Refining Operations

J. A. E. MOY, *Petroleum*, 1962, **25**, (5), 150-155

The use of Pt and base metal catalysts in many processes currently employed in petroleum refining is described. Types of operation discussed include reforming, isomerisation, cracking, hydrocracking, hydrotreating, and treatment by chemicals. (60 references)

#### Paraffin Isomerisation with Hydrogen Chloride-Promoted Dual Function Catalysts

O. H. THOMAS, J. MOOI, R. S. BARTLETT and R. A. SANFORD, *Ind. Eng. Chem. (Process Design & Development)*, 1962, **1**, (2), 116-120

The hydro-isomerisation of *n*-C<sub>4</sub>H<sub>10</sub>, *n*-C<sub>6</sub>H<sub>12</sub>, and *n*-C<sub>8</sub>H<sub>14</sub> was investigated in the temperature range 550°-750°F using Pt/Al<sub>2</sub>O<sub>3</sub>, Pt/B<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, Pd/Al<sub>2</sub>O<sub>3</sub>, Pd/B<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, Pt/SiO<sub>2</sub>, and Pt/C catalysts with HCl as a promoter. In contrast to the Al<sub>2</sub>O<sub>3</sub>-supported catalysts, Pt/SiO<sub>2</sub> and Pt/C are not activated by HCl. Decomposition of the Al<sub>2</sub>O<sub>3</sub> support by HCl attack is prevented by the incorporation of B<sub>2</sub>O<sub>3</sub>, and catalyst activity and selectivity is maintained. Aromatic and naphthenic components present in the feed do not alter catalyst performance. The performance of a 0.6% Pt/10% B<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst is reported in detail.

#### Hydrogenation of Linolenate. VI. Survey of Commercial Catalysts

A. E. JOHNSTON, D. MACMILLAN, H. J. DUTTON and J. C. COWAN, *J. Amer. Oil Chem. Soc.*, 1962, **39**, (6), 273-276

PtO<sub>2</sub>, 5% Pt/C, 5% Pt/Al<sub>2</sub>O<sub>3</sub>, 5% Pd/C, 5% Pd/Al<sub>2</sub>O<sub>3</sub>, and various supported Ni catalysts were used in this search for catalysts with high selectivity and low isomerising properties. The ratio of hydrogenation rates for linolenate to

linoleate was determined on an equal mixture of methyl linolenate and linoleate and the percentage of *trans* esters formed was determined. Hydrogenation was carried out at room temperature with Pt and Pd catalysts and at 140°C with Ni catalysts. Pt catalysts produced lowest isomerisation, but their selectivities were lower than those of the Ni and Pd catalysts.

#### Catalysis in a Modern Petroleum Refinery

C. L. THOMAS, *Chim. & Ind.*, 1962, 87, (4), 496-506  
The processes of catalytic reforming, catalytic cracking, propylene polymerisation, alkylation, and desulphurisation are outlined and the functions of the catalysts used in them are discussed.

#### The Hydrogenation of Fatty Oils with Palladium Catalysts. VI. Hydrogenation for Margarine

M. ZAJCEW, *J. Amer. Oil Chem. Soc.*, 1962, 39, (6), 301-304

Margarine stocks were produced by the hydrogenation of various oils in the presence of 1% Pd/C or 5% Pd/C catalysts. Processing was carried out on laboratory, pilot plant, and plant scales. It is possible to produce margarines of different compositions and *trans* isomer content by varying the catalyst and the processing conditions. Tables give details of these conditions and analyses of the products.

#### Flow Adsorption Method for Catalyst Metal Surface Measurements

T. R. HUGHES, R. J. HOUSTON and R. P. SIEG, *Ind. Eng. Chem. (Process Design and Development)*, 1962, 1, (2), 96-102

In this method, which involves the measurement of chemisorption of CO, CO mixed with un-adsorbed helium as a carrier is passed over the pre-reduced catalyst. The concentration of CO in the effluent gas is measured by a radioactive tracer method. Applications in the study of Pt reforming catalysts and of Rh/Al<sub>2</sub>O<sub>3</sub>, Ni/Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> are described. The method was used to study the effect of Pt content and support surface on CO chemisorption and Pt particle size, the relationship between metal surface and catalytic activity, and sintering effects.

#### Development of a Catalyst for the Elimination of Acetylene from an Ethane-Ethylene Fraction by Means of Selective Hydrogenation

H. BLUME, J. MÜNZING and H. STÜRTZ, *Chem. Techn.*, 1962, 14, (4), 214-221

Experimental work leading to the production of a Pd/Al<sub>2</sub>O<sub>3</sub> catalyst suitable for the gas-phase hydrogenation of the C<sub>2</sub>-fraction is described. Properties of the catalyst (VEB Leuna-Werke "Walter Ulbricht" 7746) are given in detail and its performance is compared with that of similar catalysts developed in the U.S.A. (26 references)

#### Reaction of Ethane with a Clean Rhodium Film

R. W. ROBERTS, *Trans. Faraday Soc.*, 1962, 58, (6), 1159-1169

Rh films of thickness 10 to 180Å were prepared by evaporating a small coil of 0.005 in. diam. pure Rh wire in the centre of a Pyrex reaction vessel under high vacuum conditions. Experiments showed that C<sub>2</sub>H<sub>6</sub> decomposes on such films at temperatures as low as 0°C to give CH<sub>4</sub> and a hydrocarbon residue adsorbed on the film. The activation energy for the disappearance of C<sub>2</sub>H<sub>6</sub> is 15 ± 1 kcal/mole. Oxygen adsorbed on a clean Rh film inhibits the cracking of C<sub>2</sub>H<sub>6</sub>. The mechanism of the cracking reaction is discussed.

#### Variation of Catalytic Properties in the Decomposition of Formic Acid on Platinum and the Effect of Adsorbed Gases

L. RIEKERT, *Z. Elektrochem.*, 1962, 66, (3), 207-222

Experiments with electrically-heated Pt wires showed that if the contact temperature is kept below 600°C, the catalytic activity of the Pt decreases during the reaction. The initial activity and its rate of decrease depend on the previous history of the catalyst. Kinetic results obtained are explained by the assumption that the irreversible adsorption of oxygen or hydrogen affects the rates of the various transformations of the substrate occurring simultaneously on the Pt surface.

#### Pyrimidines VI. A Study of the Nuclear Reduction of Certain Pyrimidines

H. AFT and B. E. CHRISTENSEN, *J. Org. Chem.*, 1962, 27, (6), 2170-2173

Adams' (PtO<sub>2</sub>), Pd/BaSO<sub>4</sub>, and 10% Pd/C catalysts were used in the nuclear reduction of chloro-, amino-, and methylpyrimidines and their chloro derivatives in acid media. It was found that hydrogenation ceases after consumption of sufficient hydrogen for the conversion to the corresponding 3, 4, 5, 6-tetrahydro-pyrimidine. The tetrahydropyrimidines may be isolated as the picrate derivatives in low yields. The nuclear reduction products are unstable in aqueous media.

#### The Activation of Platinum Catalysts by Rare Earth and Other Oxides in the Decomposition of Hydrogen Peroxide

E. B. MAXTED and S. M. ISMAIL, *J. Chem. Soc.*, 1962, (Jun.), 2330-2333

The activity in the decomposition of aqueous H<sub>2</sub>O<sub>2</sub> of a constant amount of Pt supported on various metallic oxides was measured at 20°C and 1 atm. With each support, the activity of the catalyst reached a maximum and then decreased on increasing the amount of oxide. The activities of the oxide promoters investigated was in the order: ThO<sub>2</sub> > ZrO<sub>2</sub> > Cr<sub>2</sub>O<sub>3</sub> > CeO<sub>2</sub> > MgO > TiO<sub>2</sub> > V<sub>2</sub>O<sub>5</sub> > La<sub>2</sub>O<sub>3</sub> > Pr<sub>6</sub>O<sub>11</sub> > Tl<sub>2</sub>O<sub>3</sub> > Sm<sub>2</sub>O<sub>3</sub>. In many cases the activity of the supported Pt

was considerably greater than that of unsupported Pt. Activation by two-component and three-component oxide support systems was also studied.

#### Rhodium Catalysed Nuclear Hydrogenation of $\alpha$ -Substituted Benzyl Alcohols and Ethers. A Useful Procedure for Establishing Configurations

J. H. STOCKER, *J. Org. Chem.*, 1962, 27, (6), 2288-2289

Hydrogenation of several  $\alpha$ -substituted benzyl alcohols and ethers was achieved at room temperature and a hydrogen pressure of 3-4 atm with the use of a 5% Rh/Al<sub>2</sub>O<sub>3</sub> catalyst.

#### The Detoxication of Palladium Catalysts Poisoned by Various Metallic Ions

E. B. MAXTED and S. I. ALI, *J. Chem. Soc.*, 1962, (Jul.), 2796-2801

The reactivation of Pd and Pd/ThO<sub>2</sub> catalysts poisoned by Zn-, Cd-, Pb-, Hg-, and As-containing ions adsorbed on their surface was studied. The activity of treated catalysts was compared with that of unpoisoned catalysts for the hydrogenation of cyclohexene in C<sub>2</sub>H<sub>5</sub>OH at 20°C. Methods of treatment included (i) washing with H<sub>2</sub>O, CH<sub>3</sub>CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>, dilute CH<sub>3</sub>COOH, and C<sub>2</sub>H<sub>5</sub>OH, (ii) treatment with cyclohexene, and (iii) treatment with diethyl sulphide.

#### Selective Poisoning of the Catalyst in the Rosenmund Reaction

S. AFFROSSMAN and S. J. THOMSON, *J. Chem. Soc.*, 1962, (May), 2024-2029

The effect of sulphur-containing poisons on yields of C<sub>6</sub>H<sub>5</sub>CHO produced by the hydrogenation in C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> of C<sub>6</sub>H<sub>5</sub>COCl over a Pd/BaSO<sub>4</sub> catalyst was studied at 110°C and 1 atm. There is no apparent correlation between the size of a poison molecule and its effectiveness in preventing hydrogenation beyond the aldehyde stage. Of the poisons studied, tetramethylthiourea was the most effective. It is concluded that the Rosenmund reaction is a consecutive hydrogenation, and a selective-poisoning mechanism is proposed.

#### The Catalytic Isomerisation of Alkanes

M. A. RASCHENZWA and H. M. MINATSCHEW, *Chem. Techn.*, 1962, 14, (5/6), 375 (Abstract of paper presented at the Petroleum Conference, Budapest, April 1962)

The properties of six Pd/Re/Al<sub>2</sub>O<sub>3</sub> catalysts were investigated. In the isomerisation of C<sub>6</sub>H<sub>14</sub> under optimum conditions the catalyst performance varied according to the method of preparation. Up to 52% *iso*-C<sub>6</sub>H<sub>14</sub> was produced in the presence of 1% Pd/Al<sub>2</sub>O<sub>3</sub> or 1% Pd/1% Re/Al<sub>2</sub>O<sub>3</sub> catalysts treated with H<sub>2</sub>S. The addition of 1% Re to Pd/Al<sub>2</sub>O<sub>3</sub> treated with H<sub>2</sub>S increases its stability. 48% isomerisation of C<sub>6</sub>H<sub>12</sub> was achieved with the Pd/Re/Al<sub>2</sub>O<sub>3</sub> catalyst.

#### Cyclohexane

H. W. HAINES, *Ind. Eng. Chem.*, 1962, 54, (7), 23-30

The production and industrial uses of cyclohexane are discussed. Commercial processes for the hydrogenation of C<sub>6</sub>H<sub>6</sub> to cyclohexane which are described include the U.O.P. process in which a Pt catalyst is employed.

#### Catalytic Hydrogenation of Nitrosamines to Unsymmetrical Hydrazines

G. W. SMITH and D. N. THATCHER, *Ind. Eng. Chem. (Product Res. & Dev.)*, 1962, 1, (2), 117-120

An inorganic or organic salt was added to the reaction mixture in the hydrogenation of various nitrosamines in the presence of 10% Pd/C, 10% Pt/C, and 5% Rh/C. In all cases, salt addition suppressed conversion to the corresponding amine, but the effect was less marked with Rh/C catalysts. The salts used included LiCl, CaCl<sub>2</sub>, LaCl<sub>3</sub>·7H<sub>2</sub>O, (CH<sub>3</sub>)<sub>4</sub>NBr and MgSO<sub>4</sub>, and the solvents were H<sub>2</sub>O or H<sub>2</sub>O/alcohol. The effects of temperature and pressure on the course of the reaction were studied. The hydrogenation mechanism is discussed.

#### Spectrophotometry and Light Scattering on Supported Platinum

P. DEBYE and B. CHU, *J. Phys. Chem.*, 1962, 66, (6), 1021-1027

An immersion technique was used to measure transmission and scattering for visible light of dispersed Pt on an Al<sub>2</sub>O<sub>3</sub> support. The nature of the dispersed Pt was deduced from the extinction coefficient and the increase in the refractive index of the Al<sub>2</sub>O<sub>3</sub> due to dispersion of Pt at its surface. It was assumed that part of the Pt was in an "atomic" state.

#### Interaction of Hydrocarbons with Platinum/Alumina in the Presence of Hydrogen and Helium

J. C. ROHRER and J. H. SINFELT, *J. Phys. Chem.*, 1962, 66, (6), 1193-1194

The activity of 0.3% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst for the dehydrogenation of methylcyclohexane to C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> and the dehydrocyclisation of *n*-C<sub>7</sub>H<sub>16</sub> to C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> was determined in the presence of hydrogen and helium carrier gases. In both cases, the initial catalytic activity was lower in the presence of helium than in hydrogen. Catalytic activity was largely regained on changing the carrier gas from helium to hydrogen. The role of hydrogen in maintaining the activity of the catalyst surface is discussed.

#### The Catalytic Exchange with Deuterium of Polymethylcyclopentanes on Metal Films. Evidence for $\pi$ -Bonded Intermediates

F. G. GAULT, J. J. ROONEY and C. KEMBALL, *J. Catalysis*, 1962, 1, (3), 255-274

The catalytic exchange reaction on films of Rh, Pd, Pt, and Ni was studied by a mass-spectro-

metric technique, and *cis-trans* isomerisation was investigated by gas-liquid chromatographic analysis of the reaction products. A new mechanistic theory involving the formation of  $\pi$ -bonded as well as  $\sigma$ -bonded intermediates is supported by experimental results.  $\pi$ -bonding is most evident with Pd films. Although Rh is the most active of the metals for the exchange reactions,  $\sigma$ -bonded intermediates predominate at lower temperatures. As with both Pt and Ni films,  $\pi$ -bonding increases with rise of temperature. (27 references)

## ELECTRICAL ENGINEERING

### The Conductivity of Oxide Cathodes Part 12. Influence of Strontium Ion Migration on Matrix Conductivity

G. H. METSON, *Proc. Instn. Elect. Engrs., Part C*, 1962, **109**, (15), 138-145

The migration of Sr was studied in an S-type assembly having pure Pt cores and a Ba-Sr oxide matrix. It was shown that positive Sr ions migrate in an electric field to the Pt cathode core, forming a Sr-Pt alloy. The positive ions are mobile in a low electric field at 550°K and are unable to diffuse in a concentration gradient below 800°K. Excessive concentration of Sr ions results in an increase in matrix resistivity.

## TEMPERATURE MEASUREMENT

### Reference Tables for 40 Per Cent Iridium-60 Per Cent Rhodium Versus Iridium Thermocouples

G. F. BLACKBURN and F. R. CALDWELL, *J. Res. Nat. Bur. Stds., Part C*, 1962, **66C**, (1), 1-12

The method of calibrating Ir : 40% Ir-Rh thermocouples is described in detail. Temperatures up to 2500°F were measured in a Pt-wound furnace by a Pt : 10% Rh-Pt thermocouple. In the temperature range 1950°-3800°F, calibration was carried out in an induction furnace which contained an Ir cylinder blackbody, and an

optical pyrometer was used for temperature measurement. Tables are given which relate e.m.f.s in mV with temperatures in degrees F from 32° to 3800°F and with temperatures in degrees C from 0° to 2100°C.

### A New Method for the Determination of Temperature from the Resistance of a Standard Platinum Resistance Thermometer

S. ALTENBURGER, *Feingeräte Techn.*, 1962, **11**, (3), 116-117

The method described for the determination of temperatures in the range 0° to 630.5°C requires the knowledge of resistance values of the Pt resistance thermometer at only three fixed points. The calculation of thermometer constants and the measurement of resistance at the ice-point are unnecessary.

### A Note on Platinum: Platinum-Rhodium Thermocouple Uncertainty

W. E. BOSTWICK, *I.R.E. Trans. Nucl. Sci.*, 1962, **NS-9**, (1), 253-259

Results are given of tests carried out to determine the effect different types of junction have on the "uncertainty" of temperature measurement of Pt : 10% Rh-Pt thermocouples in the range 1500° to 2800°F. Crimped, twisted, hydrogen arc-welded and resistance welded junctions were investigated. Hydrogen-arc welding was found to be unsatisfactory.

### Thermocouple Materials

F. R. CALDWELL, *Nat. Bur. Stds. Monograph 40*, Mar. 1, 1962, 43 pp.

Materials considered for thermocouple wires include noble metals and their alloys, base metals and their alloys, refractory metals, carbon and carbides. Among the noble metal combinations described are Pt : Rh-Pt, Rh-Pt : Rh-Pt, Ir : Ir-Rh, Pd : Ir-Pt, and Au-Pd : Au-Pt-Pd. Pertinent chemical, physical and mechanical properties of the separate elements are given and limitations of the thermocouple wires as to range, stability and accuracy are discussed. (128 references)

## NEW PATENTS

### Platinum-alumina Catalyst

AMERICAN CYANAMID CO. *British Patent 894,412*

A platinum-alumina reforming catalyst having improved crush strength retentive properties is made by commingling dried ageing alumina, capable of conversion to eta alumina on calcination, with a platinum compound and aluminium chloride, drying the mixture, forming it into pellets and calcining the pellets. The platinum compound is present in proportion of 0.05-1% of

platinum based on dry wt. of catalyst and the aluminium chloride in proportion of 0.25-2.5%.

### Fuel Cell

GENERAL ELECTRIC CO. *British Patent 894,530*

A combination electrode structure and electrolyte for a fuel cell is formed of a hydrated ion exchange resin membrane having a gas adsorbing metal electrode embedded in each of the two major surface layers of the membrane. The electrode