

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Oxidative Dissolution of Platinum and Ruthenium from Various Base-Metal Binary Alloys

R. L. PAUL and M. M. KRÜGER, *S. Afr. J. Chem.*, 1984, **37**, (3), 116-120

The preparation of several binary alloys composed of Pt or Ru with a base metal (Al or Fe) and leaching tests on them in HCl acid are described. The poor dissolution observed for Ru is attributed to the strong affinity of this metal for O, which results in partial passivation of the metal. The almost quantitative dissolution of the Pt alloys is ascribed to the lesser affinity of Pt for the adsorption of O, and to the presence of absorbed H.

The Effect of Various Additional Elements on Properties of Fe-Pt Permanent Magnets Having High Energy Product

K. WATANABE and H. MASUMOTO, *J. Jpn. Inst. Met.*, 1984, **48**, (9), 930-935

The effects of Rh, Pd, Ir, Ti, V, Au, Al, Ga and Ge on Fe-Pt alloys were evaluated. The permanent magnetic properties of Fe-Pt alloys can be improved by adding a small amount of Ti and V. The alloy 60at.%Fe-39at.%Pt-1at.%Ti has the highest maximum energy product of 165 kJ/m³, coercive force of 360A/m and residual flux density of 1.0T when aged at 823K after water quenching. Alloy 60.5at.%Fe-38.5at.%Pt-1at.%V showed the highest coercive force of 410kA/m, maximum energy product 160kJ/m³ and residual flux density of 1.04T when aged at 773K after water-quenching. The permanent magnetic properties cannot be improved by other additions.

A Photoemission Study of the Oxidation of Platinum in Pt-Based Alloys: Pt-Pd, Pt-Ru, Pt-Ir

L. HILAIRE, G. DIAZ GUERRERO, P. LÉGARÉ, G. MAIRE and G. KRILL, *Surf. Sci.*, 1984, **146**, (2/3), 569-582

A photoemission technique was used to study the surface composition of Pt-Pd, Pt-Ru and Pt-Ir alloys. The samples were exposed to O₂ at atmospheric pressure and 200-600°C. O-induced changes of surface composition were followed. Oxidation properties of Pt, Pd, Ru and Ir changed on alloying. The Pt-based alloys could be oxidised provided the Pd, Ru or Ir surface concentration was higher than a limit between 13% and 20% for all three systems. Above this limit, the impurity and the Pt atoms were both oxidised. Three different Pt oxidation states were detected PtO, α -PtO₂ and β -PtO₂. In the low impurity content range, neither impurity nor Pt could be oxidised.

On the Electrical Resistivity of Pt₃Fe_xMn_{1-x} Alloys in the Exchange Inversion Region

Y. V. YAKHMI, I. K. GOPALAKRISHNAN and R. M. IYER, *J. Phys. Lett.*, 1984, **45**, (16), L-781-L-784

The electrical resistivity ρ as a function of temperature is reported for a series of Pt₃Fe_xMn_{1-x} alloys with x = 0, 0.5, 0.6, 0.7, 0.8 and 1.0. The $\rho(T)$ curve for Pt₃Fe_{0.6}Mn_{0.4} shows two ρ -anomalies, one is attributed to the Curie temperature and the other to the transition to a heterogeneous non-colinear magnetic structure.

Low Voltage Hydrogen Plasma Interaction with Palladium Surface

T. D. RADJABOV, L. YA. ALIMOVA and A. V. SHARUDO, *J. Nucl. Mater.*, 1984, **125**, (3), 326-329

H₂ penetration, distribution and content in Pd under low voltage glow discharge plasma, depending on plasma component structure (H₂, He, Ar and their mixtures), irradiation succession and possible surface structure changes have been investigated by various techniques. The dependence of the H₂ permeability through Pd membranes upon the plasma component structure and the preliminary irradiation dose in the inert gas atmosphere has been shown.

On the Friction and Closing Behaviour of Gold and Palladium Alloys. Part 2. The Palladium Alloy System

H. AKPOLAT, H. G. FELLER and P. VEILE, *Metallberflaeche*, 1984, **38**, (10), 448-454

Alloys and sandwich systems based on Pd, with a disc-pin-arrangement were investigated. Friction, rubbing, roughness and surface composition were determined. The results showed a phase, in which the mechanical properties and the dominance of the 4 closing mechanisms changed continuously. All the Pd-Ni layers had selective oxidation of Ni already at 373K, and Ni enriched the surface as Ni oxide.

Some Properties of Amorphous Pd-Si and Pd-Ni-Si Alloys under Hydrogen Pressures of up to 2GPa

S. M. FILIPEK, A. W. SZAFRANSKI and F. DUHAJ, *J. Less-Common Met.*, 1984, **101**, 299-304

The electrical resistance and thermoelectric power of amorphous Pd₈₅Si₁₅, Pd₈₃Si₁₇, Pd₈₂Si₁₈, Pd₇₂Ni₁₀Si₁₈, Pd₆₃Ni₂₀Si₁₈ and Pd₅₀Ni₃₂Si₁₈ were measured as functions of the hydrogen pressure up to 2GPa. Hysteresis was observed during absorption-desorption cycling for all the Pd-Si alloys and for Pd₇₂Ni₁₀Si₁₈. Both Pd₈₅Si₁₅ and Pd₈₃Si₁₇ became saturated with H at H : Pd ratios of 0.45 and 0.36, respectively, and then exhibited superconducting behaviour with T_c = 1.6K.

Formation of Bulk Metallic Glass by Fluxing

H. W. KUI, A. L. GREER and D. TURNBULL, *Appl. Phys. Lett.*, 1984, **45**, (6), 615-616

Bulk specimens (0.4-4g) of Pd₄₀Ni₄₀P₂₀ have been undercooled consistently to the glass state with no detectable superficial crystallinity in a molten flux of dehydrated B oxide. The minimum dimensions of the most massive glass specimen so formed was 1.0cm.

On the Structure of Metallic Glasses in the System Palladium with Magnesium, Zinc or Cadmium as Second Component and Phosphorus or Arsenic as Third Component

M. EL-BORAGY, M. ELLNER and B. PREDEL, *J. Less-Common Met.*, 1984, **102**, (1), 67-78

The preparation of various metallic glasses was carried out by the splat cooling method. Phase diagrams of the binary and ternary systems are presented. The ranges of good glass-forming ability are outside 80 : 20 stoichiometry.

Magnetic Properties of Intermetallic Compounds RhMnGe, PdMnGe, Pd_{1.5}Mn_{0.5}Si, Pd_{1.5}Mn_{0.5}Ge and RhMnSi

W. BAZELA, *J. Less-Common Met.*, 1984, **100**, 341-346

The magnetic properties of the polycrystalline title compounds were studied using magnetometric measurements. The first four compounds display ferromagnetic properties at low temperatures, whereas RhMnSi is an antiferromagnet. Their Curie (Néel) temperatures are 622K, 576K, 498K, 392K and 400K, respectively and their magnetic moments are 3.56μ_B, 3.165μ_B, 2.12μ_B, 1.6μ_B and 2.6μ_B.

Mobility of Pd and Si in Pd₂Si

E. C. ZINGU, J. W. MAYER, C. COMPIE and R. PRETORIUS, *Phys. Rev. B*, 1984, **30**, (10), 5916-5922

A diffusion-membrane technique has been developed to determine the mobilities of Pd and Si in Pd₂Si. A multilayer film structure Pd/Pd₂Si/Ge, in which Ge acts as a sink for Pd is used to monitor the flux of Pd through Pd₂Si. The Si flux is determined by using the thin film structure Si/Pd₂Si/Cr in which Cr acts as a sink for Si. Values for the Pd and Si mobilities were calculated and good agreement was found between the calculated Pd mobility values and the parabolic rate constant for Pd₂Si growth around 200°C.

Profile of Crude Rhodium

H. RENNER and U. TRÖBS, *Metall*, 1984, **38**, (10), 1002-1005

The history of platinum group metals and properties of Rh are explained. Then the geological occurrence of Rh and other platinum group metals is discussed. Present prices of platinum group metals and means of recycling them are given. The recovery of Rh and platinum group metals, the applications and uses of Rh are commented on.

Relationship between the Crystal Structure and the Reentrant Superconducting Properties of (Sn_{1-x}Er_x)Er₄Rh₆Sn₁₈

S. MIRAGLIA, J. L. HODEAU, M. MAREZIO, H. R. OTT and J. P. REMEIKA, *Solid State Commun.*, 1984, **52**, (2), 135-137

Single crystals of (Sn_{1-x}Er_x)Er₄Rh₆Sn₁₈ are superconducting (T_c = 1.3K) for x ~ 0, and are reentrant superconductors (T_c = 1.24K and T_m = 0.34K) for x ~ 0.30 and undergo a single magnetic transition (T_m = 0.68K) for x ~ 0.75. Since the occupancy of the [Sn(1)_{1-x}Er(1)_x]Er(2)₄ sublattice is responsible for the variation of the low temperature properties, predictions can be made as to new reentrant superconductors in the MRh_xSn_y series (M = RE). This seems to be the first system of reentrant superconductors where stoichiometry within a sublattice controls both magnetic ordering and superconductivity.

Magnetic Properties of New Ternary Silicides: Tb₂Ir₃Si₅ and Both Polymorphic Forms of TbIr₂Si₂

M. HIRJAK, B. CHEVALIER, J. ETOURNEAU and P. HAGENMULLER, *Mater. Res. Bull.*, 1984, **19**, (6), 727-733

New ternary silicide Tb₂Ir₃Si₅ and two polymorphic forms of TbIr₂Si₂ have been prepared. The three compounds order antiferromagnetically. A high Néel temperature is observed for the low-temperature modification (T_N = 80K, θ_p = 42K). Tb₂Ir₃Si₅ and the high temperature modification of TbIr₂Si₂ have low T_N and θ_p values.

Semiconducting Behaviour of RuGa₂

J. EVERS, G. OEHLINGER and H. MEYER, *Mater. Res. Bull.*, 1984, **19**, (9), 1177-1180

RuGa₂, with TiSi₂ type structure was prepared by inductively heating Ru and Ga in a water cooled Cu boat under Ar. The electrical conductivity of a polycrystalline sample 7 × 5 × 4mm³ was measured from 20-400°C by the four point technique. RuGa₂ is a semiconductor with electrical resistivity of 0.2Ωcm at room temperature. RuAl₂ and Os₂Si₃ were also shown to have semiconducting properties.

Effect of Atmosphere on the Electrical Conductivity of RuO₂ and Ruthenate Layers

B. ŘEMÁK, M. FRUMAR and L. KOUDELKA, *J. Mater. Sci. Lett.*, 1984, **3**, (11), 1011-1014

The effects of N₂ and O₂ on the electrical conductivity of polycrystalline layers of RuO₂ and Bi₂Ru₂O₇ pure and doped with an excess of Bi₂O₃ and RuO₂ was studied over a broad temperature range. The electrical resistance of Bi₂Ru₂O₇ layers and ruthenate layers with excess RuO₂ and Bi₂O₃ in the range 20-650°C changes very little, but above 650°C it decreases more steeply. The temperature dependence of resistance of the thick layers of pure RuO₂ has a similar shape. N₂ exposure increases the resistance of the layers, changing to O₂ decreases it.

The Micro-Structure of RuO₂ Thick Film Resistors and the Influence of Glass Particle Size on Their Electrical Properties

T. INOKUMA, Y. TAKETA and M. HARADOME, *IEEE Trans. Components, Hybrids Manuf. Technol.*, 1984, **CHMT-7**, (2), 166-175

The microstructure and electrical properties of RuO₂ thick film resistors have been studied with emphasis on the effects of material parameters and processing variables, such as size of glass frit particles, RuO₂:glass mixing ratio, firing conditions, etc. A network of RuO₂ develops in a glass matrix on firing, and the increase in the glass particle size enlarged the cell in the network without any significant change in the microstructure.

CHEMICAL COMPOUNDS

Fluorosulfates of the Noble Metals. 5. Fluorosulfato Derivatives of Platinum(IV) and the HSO₃F-Pt(SO₃F)₄ Superacid System

K. C. LEE and F. AUBKE, *Inorg. Chem.*, 1984, **23**, (14), 2124-2130

A simple synthetic route to pure Pt(SO₃F)₄ is described. This compound was found to be an excellent fluorosulphate ion acceptor forming either [Pt(SO₃)F₆] or an oligomeric anion of the composition [Pt(SO₃F)₅]⁻. A number of complexes with the counterions Cs⁺, ClO₂⁺, Ba²⁺ and Br₃⁻ were prepared and spectroscopically characterised. The novel dibasic acid H₂[Pt(SO₃F)₆] which undergoes dissociation equilibria was formed in a solution of HSO₃F.

Preparation and Characterization of Some Ruthenium (III) Porphyrins, Including the Crystal Structure of Bromo(octaethylporphinato)(triphenylphosphine)ruthenium(III)

B. R. JAMES, D. DOLPHIN, T. W. LEUNG, F. W. B. EINSTEIN and A. C. WILLIS, *Can. J. Chem.*, 1984, **62**, (7), 1238-1245

Some Ru(III) complexes Ru(porp)(L)X and [Ru(porp)L₂]X, (porp = dianion of octaethylporphyrin (OEP) or tetraphenylporphyrin (TPP)), (L = PPh₃, P¹¹Bu₃; X = Br, Cl) were prepared from the precursor complexes Ru(porp)L₂ or Ru(porp)(CO)L using as oxidant the halogens or air. The X = PF₆ salts can be made using Et₂O⁺PF₆⁻ as oxidant, Ru(II) porphyrin π-cation radical intermediates have sometimes been detected.

Preparation and Electrical Conductivity of Bi₂Ru₂O₇ Single Crystals

B. ŘEHÁK, K. HOŘCIC, M. FRUMAK and L. KOUDELKA, *J. Cryst. Growth*, 1984, **68**, (2), 647-649

Single crystals of Bi₂Ru₂O₇ have been grown by the flux method from a Bi₂O₃/V₂O₅ melt. The electrical conductivity of the crystals is of a metallic type, and the major current carriers are electrons.

ELECTROCHEMISTRY

The Catalytic Thermal Decomposition of Water and the Production of Hydrogen

H. H. G. JELLINEK and H. KACHI, *Int. J. Hydrogen Energy*, 1984, **9**, (8), 677-688

The Pt and Ir catalysed thermal decomposition of H₂O has been carried out at 1300-1400°C. The dissociation was very rapid, yielding appreciable quantities of H₂ and O₂. The great rate of catalytic decomposition compensated for the small degrees of thermal decomposition in this temperature range. Two prototypes for large scale thermal H₂ production are proposed and are described in detail. A reasonable number of these prototypes can replace one year's supply of natural gas by H₂ in the U.S.A.

Oxygen Reaction on Titanium Catalysed by Gold, Platinum and Palladium

R. ZEJNILOVIĆ, M. PJEŠČIĆ, M. ŠLJUKIĆ and A. R. DESPIĆ, *J. Appl. Electrochem.*, 1984, **14**, (4), 481-488

The electrocatalytic properties of Ti surfaces coated with small amounts (0.025-0.6mg/cm²) of Pt, Pd and Au and their mixtures, have been investigated during O₂ evolution and reduction in alkaline solution. All the samples had higher electrochemical activity than the corresponding compact metal surfaces, which may be ascribed to a larger specific surface area of the dispersed catalysts than of smooth metal surfaces. Dispersed Pd gave the best performance, the potential gap between O₂ evolution and reduction at 1mA/cm² being reduced to 0.66V. No indication of a fast degradation was found.

The State of Pd(II) in Solutions of Sulphuric Acid

E. S. RUDAKOV, A. P. YAROSHENKO, R. I. RUDAKOVA and V. V. ZAMASHCHIKOV, *Ukr. Khim. Zh. (Russ. Ed.)*, 1984, **50**, (7), 680-684

Spectrophotometric studies of the state of Pd(II) in H₂SO₄ solutions showed that Pd(II) is found either as aqueous-ions or as monobisulphate complexes. Stability constants of the complexes in the solution H₂SO₄ + HClO₄ with specific concentration of 8.00 are given at 25 and 80°C. It is shown that aqueous-ions and monobisulphate Pd(II) complexes in H₂SO₄ react with H₂ at the same rate.

Electrochemical Polarisation of Dispersed Palladium Selenide in Caustic Soda Solutions

A. BAESHOV, M. Z. UGORETS, O. I. SEMINA and D. N. NAGUMANOV, *Zh. Prikl. Khim. (Leningrad)*, 1984, **57**, (7), 1520-1524

Electrochemical polarisation studies of dispersed Pd selenide made in 4M NaOH at 25°C showed the solid phase reduction of Pd and the electrochemical decomposition of Se into the solution as selenides. The rate of electrochemical decomposition of Pd selenide into NaOH solution was fast and was complete when accompanied by oxidation processes.

Electrochemistry of Coordination Compounds. Part XXI. Electrogeneration and Decay of Rh(PPh₃)₃ and Rh(PPh₃)₄

G. ZOTTI, S. ZECCHIN and G. PILLONI, *J. Electroanal. Chem. Interfacial Electrochem.*, 1984, 175, (1/2), 241-250

The voltammetric behaviour of Rh(PPh₃)₃(DME)(ClO₄) was studied in 1,2-dimethoxyethane (DME) at the Pt electrode. The formally three-co-ordinate d⁸ species is reduced in two one-electron reversible processes. The d⁹ intermediate, Rh(PPh₃)₃, either undergoes a fast second order reaction producing the dimers [Rh(PPh₃)₄]₂ and [Rh(PPh₃)₂]₂ or co-ordinates one extra phosphine ligand if present, followed by dimerisation.

In-situ Identification of RuO₄ as the Corrosion Product during Oxygen Evolution on Ruthenium in Acid Media

R. KÖTZ, S. STUCKI, D. SCHIERSON and D. M. KOLB, *J. Electroanal. Chem. Interfacial Electrochem.*, 1984, 172, (1/2), 211-219

The corrosion of Ru during O₂ evolution in 0.5M H₂SO₄ was studied using cyclic voltammetry, the rotating ring-disc electrode technique and differential reflectance spectroscopy. Cyclic voltammetric curves show a distinct reduction peak at ~ + 0.80V vs. S.C.E. in the negative scan provided the positive limit is extended beyond ~ + 1.2V vs. S.C.E. The voltammetric feature observed at ~ + 0.80V vs. S.C.E. is attributed to the reduction of RuO₄ in solution. It is concluded that the onset of O₂ evolution and Ru corrosion takes place at the same potential and thus the reaction pathways of both processes involve a common intermediate.

PHOTOCONVERSION

Hydrogen Evolution and Iodine Reduction on an Illuminated n-p Junction Silicon Electrode and Its Application to Efficient Solar Photoelectrolysis of Hydrogen Iodide

Y. NAKATO, Y. EGI, M. HIRAMOTO and H. TSUBOMURA, *J. Phys. Chem.*, 1984, 88, (19), 4218-4222

A p-Si electrode, highly doped with P from the surface (n⁺/p-Si) generated a photocurrent corresponding to I (or triiodide) reduction in a HI/I₂ solution at potentials much more positive than those on Pt and p-Si electrodes. The kinetics of the H₂ photoevolution were improved by depositing a 0.5-3nm Pt layer on the surface, but the H₂ evolution photocurrent gradually decayed under prolonged illumination, and was restored by keeping the electrode in an oxidative condition. Photoelectrochemical cells, with a Pt-deposited n⁺/p-Si electrode and a Pt counterelectrode electrolysed HI into H and triiodide ions under no externally applied voltage with a high solar to chemical energy conversion efficiency of 7.8% under simulated solar AM 1 radiation.

Photoproduction of Hydrogen by Dye-Sensitized Systems

Z.-C. BI and H. TI TIEN, *Int. J. Hydrogen Energy*, 1984, 9, (8), 712-722

Visible light induced production of H₂ has been investigated in five different systems. Acridine yellow/EDTA/K₂PtCl₆ was shown to be the best system examined, and when Triton X-100, a non-ionic interface agent, was added there was a further enhancement in the rate of H₂ evolution.

Photogenerated Catalysis by Transition-Metal Complexes. Photoacceleration of the Valence Isomerization of Quadricyclene to Norbornadiene in the Presence of PdCl₂(η⁴-norbornadiene)

N. BORSUB and C. KUTAL, *J. Am. Chem. Soc.*, 1984, 106, (17), 4826-4828

Light accelerates the rates at which PdCl₂(η⁴-NBD)(I) catalyses the valence isomerisation of quadricyclene (Q) to norbornadiene (NBD). The observed quantum yield, defined as (mol of NBD produced/mol of photon absorbed), can exceed 10² and is dependent upon Q concentration, light intensity and solvent.

Photocatalytic Dehydrogenation of Propan-2-ol Using Rhodium Based Catalysts

C. G. GRIGGS and D. J. M. SMITH, *J. Organomet. Chem.*, 1984, 273, (1), 105-109

Efficient photogeneration of H₂ from propan-2-ol can be achieved with a number of preformed Rh^I complexes, as well as RhCl₃ in the presence of Ph₃PO or Ph₃P after exposure to air. The turnovers for the Rh^I species are in the range 2000-6000 mmol H₂/h.mmol/Rh, which are much higher than those claimed for such photolytic systems. RhCl₃ systems have lower activity (~1000 turnovers).

Effect of the Ru⁺⁺⁺ Treatment on the Electrochemical Hydrogen Evolution Reaction at GaAs Electrodes

K. UOSAKI and H. KITA, *Chem. Lett. Jpn.*, 1984, (6), 953-956

The electrochemical H₂ evolution reaction (H.E.R.) both at n-GaAs and p-GaAs electrodes in the dark was accelerated significantly by dipping treatment in RuCl₃ solution; but the photocurrents at p-GaAs decreased by the treatment. The Ru⁺⁺⁺ treatment introduces a catalytic surface for the H.E.R. and also surface states which act as recombination centres.

Redox Polymeric Film Electrode by Electropolymerization of a Pyrrole-Containing Complex of Ruthenium(II)

S. BIDAN, A. DERONZIER and J.-C. MOUTET, *Nouv. J. Chim.*, 1984, 8, (8/9), 501-503

A photosensitive electroactive electrode was obtained by anodic electropolymerisation of the [Ru(bpy)₂L₂]²⁺ complex on Pt in which L is a pyrrolic group-substituted pyridine.

Photoredox Reactions in Water-in-Oil Microemulsions. The Functions of Amphiphilic Viologens in Charge Separation and Electron Transfer across a Water-Oil Boundary

D. MANDLER, Y. DEGANI and I. WILLNER, *J. Phys. Chem.*, 1984, **88**, (19), 4366-4370

The photosensitised reduction of a series of dialkyl-4,4'-bipyridinium salts, C_nV^{2+} was examined in water-in-oil microemulsions, by using $Ru(bpy)_3^{3+}$ as sensitizer and $(NH_4)_3EDTA$ as electron donor. With the amphiphilic electron acceptors ($n = 8-18$), these microemulsion media affect the charge separation of the initial encounter cage complex $[Ru(bpy)_3^{3+} \cdots C_nV^+]$, and stabilise the photoproducts, C_nV^+ and $Ru(bpy)_3^{3+}$, against the recombination process. Consequently, enhanced quantum yields for C_nV^+ formation are observed.

ELECTRODEPOSITION AND SURFACE COATINGS

New Platinum Plating Process Ensures Numerous Fields of Application for Platinised Anodes

H. HEINER, *Galvanotechnik*, 1985, **75**, (10), 1271-1272

Platinising by electrolysis in the melt at temperatures $>500^\circ C$ in an inert gas atmosphere gives coatings which are distinguished by high adhesion, ductility and freedom from porosity. This enables platinised refractory metals, such as Ti, Nb and others to be used for manufacturing insoluble anodes for use in acid electrolytes. Their use is particularly good as expanded metal, as the actual anode surface is greater than the geometrical one.

Pulsed Current Electrodeposition of Palladium

Y. FUKUMOTO, Y. KAWASHIMA, K. MANDA and Y. HAYASHI, *Met. Finish.*, 1984, **82**, (9), 77-80

Electrodeposition of Pd from dinitrodiamine, dibromodiamine and dichlorodiamine baths has been performed by applying pulsed current electrolysis. A close correlation was found between crystallographic features of the Pd deposits and the mode of the pulse current. A decrease in grain size of the deposits was observed by using higher pulse current density, longer pulse on-time and shorter off-time which lead to higher cathodic overpotentials. Although desorption of H_2 from the Pd deposits was expected during off-time, this did not always occur.

Palladium-Nickel Coating System for High Reliability Connectors

S. W. UPDEGRAFF, *Electron. Ind.*, 1984, **10**, (9), 43, 45-46, 48

The properties which make a Pd-Ni alloy system superior to gold for application to connectors are reviewed. The Pd-Ni is plated onto square pin connectors, and then plated with gold flash.

HETEROGENEOUS CATALYSIS

Study of the Composition of Olefins Formed in Conditions of Dehydrogenation of n-Decane on Pt/Al₂O₃

G. V. ISAGULYANTS, O. D. STERLIGOV, A. P. BARKOVA, I. P. YAKOVLEV, M. A. PANFILOVA, L. K. MASLOVA and N. A. ELISSEV, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, (9), 2049-2053

The effect of catalyst composition and of the reaction conditions on the ratio of n-decene (with various positions of the double bond) formed during dehydrogenation of n-decane was studied on Pt/Al₂O₃ catalysts modified by MnO. Amount of α , cis- and trans-decene, formed during dehydrogenation of n-decane was on average in the ratio of 1:8:11, respectively, and no dependence on the catalyst composition was observed. Decenes with internal double bonds were predominantly formed.

Activity, Yield Patterns, and Coking Behaviour of Pt and PtRe Catalysts during Dehydrogenation of Methylcyclohexane. I. In the Absence of Sulfur. II. Influence of Sulfur

R. W. COUGHLIN, K. KAWAKAMI and A. HASAN, *J. Catal.*, 1984, **88**, (1), 150-162; 163-176

The conversion of methylcyclohexane decreased less rapidly while selectivity and aromatic yield increased more rapidly over a 20h period with PtRe/Al₂O₃ than with Pt/Al₂O₃. Coke deposition was retarded on the PtRe as compared to the Pt catalysts. After H₂ treatment selectivity and aromatic yield were lower for PtRe than Pt catalyst. Adding small amounts of S lowers hydrocracking for both Pt and PtRe. S retards deactivation of the dehydroaromatization activity of PtRe catalysts more significantly than for monometallic Pt catalysts.

Kinetics of the Catalytic Decomposition of Hydrogen Iodide in the Thermochemical Hydrogen Production

Y. SHINDO, N. ITO, K. HARAYA, T. HAKUTA and H. YOSHITOME, *Int. J. Hydrogen Energy*, 1984, **9**, (8), 695-700

The decomposition rates of HI over Pt/ γ -Al₂O₃ were measured in the temperature range of 480-700K by a flow method. HI decomposed to H₂ and I₂ and an overall rate equation was obtained according to the Langmuir-Hinshelwood model, assuming the rate determining step was a surface reaction.

Peculiarities in the Conversion of Naphthenes on Bifunctional Catalysts

J. WEITKAMP, S. ERNST and H. G. KARGE, *Erdoel Kohle Erdgas Petrochem.*, 1984, **37**, (10), 457-462

The differences between the reactions of naphthenes and alkanes on bifunctional catalysts are reviewed and some peculiar results from a bifunctional mordenite catalyst are examined. Ideal bifunctional catalysts are Pt/SiO₂-Al₂O₃, Pt/CaY zeolite, Pt/ultrastable Y zeolite and Pd/LaY zeolite. (39 Refs.)

Rapid Determination of Heavy Water Concentration by Isotopic Exchange Reaction between Liquid Water and Hydrogen Using Hydrophobic Platinum Catalyst

T. TAKAHASHI, S. OHOKOSHI, N. SHINRIKI and T. SATO, *Bunseki Kagaku*, 1984, **33**, (5), 233-236

A 2% Pt coated on HD4 type styrene-divinyl benzene copolymer was used as catalyst to promote the H₂-D₂ exchange reaction at room temperature and atmospheric pressure. The catalyst did not lose its activity for a long time after contact with water because it is hydrophobic. On losing its activity it can be easily reactivated. The catalyst was used in a gas chromatographic method for the rapid easy determination of heavy water in light water, in concentrations 0.01-99.5%.

Hydrogenation of Acetone to Isopropanol with High Efficiency and Selectivity at 330K over Pt-TiO₂

J. CUNNINGHAM and G. H. A. SAYYED, *Nouv. J. Chim.*, 1984, **8**, (7), 469-474

The preparation of finely dispersed Pt on TiO₂ and various pretreatments to confer high activity for selective hydrogenation of acetone vapour to isopropanol at 330K are described. With optimum values of partial pressures P_{H₂} and P_{acetone} in the Ar carrier gas 75% conversions with selectivities ≥98% were achieved and maintained. Conversion decreased with the reciprocal of the flow rate. H₂ dissociation took place at sites involving Pt and acetone attack occurred on TiO₂. Effects of differences in P_{acetone} and the temperature of pre-reduction were examined. This catalyst has enhanced catalytic activity at 330K.

n-Hexane Isomerisation and Toluene Disproportionation in the Presence of Modified Platinated Zeolites

KH. DIMITROV, R. DIMITROVA, Z. POPOVA, K.-G. SHCHAINBERG, A. PETERS and K. G. NESTLER, *Akad. Nauk SSSR, Neftekhim.*, 1984, **24**, (3), 335-339

Studies made of n-hexane isomerisation and toluene disproportionation in the presence of 0.5wt.% Pt/zeolite catalysts modified by addition of REE (REE = mixture of ~25% Pr, 55% Nd and 20% La) and of Mn²⁺ cations into CaNaY zeolite showed improved catalytic properties. Zeolites REE CaNaY were found to be active during n-hexane isomerisation and MnCaNaY zeolites during toluene disproportionation.

Kinetic Analysis of Complex Catalytic Reactions

G. F. FROMENT, *Bulg. Acad. Sci., Commun. Dep. Chem.*, 1984, **17**, (1), 28-43

Reaction rate data can be obtained in either differential or integral reactions. Examples are given for hydroisomerisation and hydrocracking of n-paraffins on a Pt/ultrastable-Y-zeolite, for catalytic cracking of gas oil on zeolites and for naphtha reforming on Pt/Al₂O₃. (55 Refs.)

Molecular Clusters. Applications in Homogeneous and Heterogeneous Catalysis

M. DORBON, *Rev. Inst. Fr. Pet.*, 1984, (4), 497-515

An overview of the metal cluster catalysts in heterogeneous and homogeneous reactions is presented. Various Pt, Pd, Rh, Os, Ir and Ru clusters and their structures and reactions are examined. A general examination of clusters in catalysis, catalysis mechanisms and Fischer-Tropsch syntheses are presented. Olefin hydrogenations and H₂ displacement from H₂O are examined. The view is taken that cluster chemistry is new and vast and that the catalytic properties of clusters have shown remarkable activity.

Oxidation of Formic Acid in Aqueous Solution of Palladium Catalysts

B. CLAUDEL, M. NUEILATI and J. ANDRIEU, *Appl. Catal.*, 1984, **11**, (2/3), 217-225

Studies of liquid phase oxidation of formic acid by O₂, both dissolved in H₂O, were made in the presence of supported and non-supported Pd catalysts at 100-150°C. Determination of diffusional limitations allows an investigation of the rate law in the chemical regime. Appreciable conversions can be reached with a Pd content as low as 50 ppm.

The Influence of High Methane Concentration on the Stability of Catalytic Flammable-Gas Sensing Elements

S. J. GENTRY and P. T. WALSH, *Sens. Actuators*, 1984, **5**, (3), 229-238

Studies were made of the effect of the form of the Pd catalyst used in catalytic flammable-gas sensing elements on their stability following exposure to high methane concentration. Improvement in stability to coking effect was achieved either by depositing Pd on a high surface-area support or by using a co-precipitation of Pd and Th. The apparent H solubilities of a series of Pd+ThO₂ elements with different Pd:ThO₂ ratios were determined by a temperature-programmed technique. The role of ThO₂ as a coke prevention agent is to decrease the Pd particle size which results in a lower rate of methane decomposition.

Reduction of NO by H₂-CO Mixtures over Silicon-Supported Rhodium: Infrared and Kinetic Studies

W. C. HECKER and A. T. BELL, *J. Catal.*, 1984, **88**, (2), 289-299

The kinetics of NO reduction by H₂-CO mixture was studied over a Rh/SiO₂ catalyst. The presence of CO retards the rate of NO reduction presumably due to competitive adsorption with H₂. The catalyst activity is 50% higher when the catalyst is preoxidised rather than pre-reduced. NH₃ formation is suppressed when the catalyst is preoxidised and a product believed to be HNCO is formed instead of urea. In situ i.r. spectra of the catalyst show that at NO conversion below 70% the surface is dominated by adsorbed NO.

Alcohol Synthesis from Syngas on Ruthenium-Based Composite Catalysts

M. INOUE, T. MIYAKE, Y. TAKEGAMI and T. INUI, *Appl. Catal.*, 1984, **11**, (1), 103-116

Hydrogenation of CO on Ru-Mo-Na and related catalysts was studied at 255°C and 86kg/cm² pressure. A series of straight chain primary alcohols, together with hydrocarbons were formed on the catalysts. A Ru-Fe-Na/Al₂O₃ catalyst had considerable activity for the formation of higher alcohols, but it gave a low alcohol selectivity. Ru-Mo-Na/active C and Ru-Mo-La/Al₂O₃ had high activity for alcohol synthesis, but 70% of this alcohol was CH₃OH. The Ru-Mo-Na/Al₂O₃ catalyst prepared from RuCl₃ was preferable to the other catalysts.

HOMOGENEOUS CATALYSIS

The Platinum Complex Catalyzed Transformation of Primary Amines to Secondary Amine

Y. TSUJI, J. SHIDA, R. TAKEUCHI and Y. WATANABE, *Chem. Lett. Jpn.*, 1984, (6), 889-890

The novel catalysis by a homogeneous Pt catalyst is described. In combination with SnCl₂·2H₂O it activates a primary amine and catalyses the transformation to secondary amine at 180°C. Dibutylamine was obtained from butylamine in 74% yield.

Tetrahedron Report Number 166: Palladium (II) - Assisted Reactions of Monoolefins

L. S. HEGEDUS, *Tetrahedron*, 1984, **40**, (13), 2415-2434

The two major reaction types of Pd(II)-complex-catalysis of olefins, the nucleophilic attack of Pd(II) complexed olefins, and insertion of olefins into σ -alkylpalladium(II) species are discussed. Nucleophiles reacted include O, N and C, whilst insertion reactions involving oxidative addition, transmetallation and "ortho-palladation" are discussed. (74 Refs.)

Regioselective Synthesis of 1-Olefins by Palladium-Catalyzed Hydrogenolysis of Terminal Allylic Compounds with Ammonium Formate

J. TSUJI, I. SHIMIZU and I. MINAMI, *Chem. Lett. Jpn.*, 1984, (6), 1017-1026

Various terminal allylic compounds, such as allylic esters, phenyl ethers, carbonates, chlorides and vinyl epoxides react with ammonium on Na formate to give 1-olefins with high regioselectivity using Pd tributylphosphine complex as catalyst.

Selective Palladium Catalysed Mono-hydroesterification of Diols

S. B. FERGUSSON and H. ALPER, *J. Chem. Soc., Chem. Commun.*, 1984, (20), 1349-1351

Olefins react with diols under oxidative carbonylation and acidic conditions, using Pd and Cu(II) chloride as catalysts, to give hydroxy esters.

Aromatic Hydroxylation: the Direct Oxidation of C-Pd into C-OPd

A. K. MAHAPATRA, D. BANDYOPADHYAY, P. BANDYOPADHYAY and A. CHAKRAVORTY, *J. Chem. Soc., Chem. Commun.*, 1984, (15), 999-1000

The C-Pd bond in cyclopalladated azobenzenes can be converted into the C-OPd function in good yield by stoichiometric reactions with m-chloroperbenzoic acid. In effect azobenzene is oxidised to 2-hydroxyazobenzene and 2,2'-dihydroxyazobenzene.

Synthesis of Esters by Rhodium (I) Catalyzed Borate Ester-Benzyl Bromide Carbonylation Reactions

J. B. WOELL and H. ALPER, *Tetrahedron Lett.*, 1984, **25**, (35), 3791-3794

Studies of the benzylic halides reaction with trialkylborates and CO in the presence of 1,5-hexadiene Rh chloride dimer showed the production of esters in excellent yields. The reaction is applicable to the synthesis of primary, secondary and even tertiary esters.

Hydroformylation of Propene Catalyzed with Carbonylchlorobis(triphenylphosphine) Rhodium (I)

M. POLIEVKA, A. JEGOROV, L. UHLAR and V. MACHO, *Collect. Czech. Chem. Commun.*, 1984, **49**, 1677-1679

The effect of amines, amino acids, N heterocyclic compounds and urea derivatives on the rate of the Rh(CO)Cl(PPh₃)₂ catalysed hydroformylation of propene was studied. A positive effect on the catalytic activity was found with modifying ligands of very low basicity.

Carbonylation with Homologation Reactions of Formic and Higher Molecular Weight Carboxylic Acid Esters with Ruthenium Catalysts

G. BRACE, G. GUALNAL, A. M. RASPOLLI, G. SBRANA and G. VALENTINI, *Ind. Eng. Chem., Prod. Res. Dev.*, 1984, **23**, (3), 409-417

The carbonylation and homologation of formic and higher molecular weight carboxylic acid esters catalysed by Ru carbonyl iodide systems at 200°C and under a CO/H₂ pressure of 15-20MPa was studied. The catalyst was active in the hydrogenation of the formyl moiety of methyl formate to methyl derivatives and in carbonylation and homologation.

Ruthenium-Catalyzed Oxidation of Alcohols and Catechols Using t-Butyl Hydroperoxide

Y. TSUJI, T. OHTA, T. IDO, H. MINBU and Y. WATANABE, *J. Organomet. Chem.*, 1984, **270**, (3), 333-341

Ru complexes catalyse the oxidation of alcohols into the corresponding ketones or aldehydes when t-BuOOH (70% aqueous) is used as an oxidant. The reactions proceed at room temperature to give the products in good yields. RuCl₂(PPh₃)₃ had the highest catalytic activity.

Water-Gas Shift Reaction over Ruthenium Carbonyl Complexes Anchored to Silica via Phosphine Ligands

Y. DOI, A. YOKOTA, H. MIYAKE and K. SOGA, *Inorg. Chim. Acta, Artic. and Lett.*, 1984, **90**, (1), L7-L9

The synthesis of Ru carbonyl complexes, anchored to SiO₂ via phosphine ligands, Ru(CO)₄(PPh₂C₂H₄-SIL)₍₁₎ and H₄Ru₄(CO)₈(PPh₂C₂H₄-SIL)₄(2), and their catalytic properties for the water gas shift reaction are reported. The i.r. spectra of both of the used catalysts were almost identical with their original complexes. Catalyst (2) could be reused without any loss of catalytic activity. Complex (1) exhibited a high catalytic activity for the water gas shift reaction.

FUEL CELLS

Functional Metal-Porphyrine Derivatives and Their Polymers. Part II. Secondary Fuel Cells based on Oxygen Reduction at a Platinum Electrode Modified by Metal-2,9,16,23-Tetracarboxyphthalocyanine Covalently Bound to Poly(2-vinylpyridine-styrene)

O. HIRABARU, T. NAKASE, K. HANABUSA, H. SHIRAI, K. TAKEMOTO and N. HOJO, *J. Chem. Soc., Dalton Trans.*, 1984, (8), 1485-1489

A new type of secondary fuel cell is described in which O₂ evolved by electrolysis of H₂O in the charging process is stored in the polymer matrix of metal-2,9,16,23-tetracarboxyphthalocyanine covalently bound to poly(2-vinylpyridine-styrene) (M = Fe^{III}, Co^{II}, Ni^{II} and Cu^{II}) on a Pt electrode and then electrocatalytically reduced in the discharging process in 30% KOH aqueous solution. For this cell, there was no significant decay in its characteristics after over 30 charge-discharge cycles.

NEW PATENTS

METALS AND ALLOYS

High Permeability Alloy

FURUKAWA ELECTRIC CO. LTD. *U.S. Patent* 4,435,212
A high permeability alloy of excellent wear resistance, suitable for use in magnetic heads, consists essentially of Fe with 3-10% Al, 4-11% Si and 2.1-20% Ru.

CHEMICAL COMPOUNDS

Ruthenium and Iridium Pyrochlores

EXXON RESEARCH & ENGINEERING CO.

U.S. Patent 4,440,670

A procedure is described for preparing electrically conductive compounds of formula M₂(M'_{2-x}M_x)O_{7-y} which have a high surface area. M is Pb and/or Bi and M' is Ru and/or Ir.

ELECTRICAL AND ELECTRONIC ENGINEERING

Enhanced Quantum Efficiency of Pd₂Si Schottky Infrared Diodes on <111> Si

R. C. MCKEE, *IEEE Trans. Electron Devices*, 1984, **31**, (7), 968-970

A two-fold improvement in the i.r. emission efficiency has been obtained on Pd₂Si/p-Si Schottky diodes through using <111> Si for the substrate orientation. Photo response measurements were taken for <111> Si and <100> Si. Leakage current vs. temperature measurements at 6V reverse bias of the Pd₂Si/p-Si <111> diodes with guard ring structures, agreed with thermionic emission current theory, using barrier value 0.35 eV obtained by photo response. These results have implications for detection applications.

TEMPERATURE MEASUREMENT

Search for Thermometers with Low Magnetoresistive Effects: Platinum-Cobalt Alloy

F. PAVESE and P. CRESTO, *Cryogenics*, 1984, **24**, (9), 464-470

A systematic set of measurements on Pt-Co thermometers of difference Co concentrations have been performed at 2-28K and up to 6T. Also three commercial thermometers with 0.5wt% Co were used. Pt-Co alloy, with 0.5at.% Co was insensitive to magnetic fields within ±0.5K down to 4K and up to 4T, or within ±0.2K above 10K and below 3T. Among high-stability thermometers presently available Pt-Co alloy showed the least error in magnetic field at fields of a few teslas.

ELECTROCHEMISTRY

Electrolysis Electrodes

PERMELEC ELECTRODE LTD. *British Appl.* 2,134,544A

Between the conductive metal substrate and electrode active coating (of a platinum group metal or its oxide) of an electrolytic electrode there is an intermediate layer comprising Pt dispersed in a conductive mixed oxide of at least one of Ti (IV) and Sn (IV) and of at least one of Ta (V) and Nb (V).

Tetrafluoroethylene Electrolytic Production

IMPERIAL CHEMICAL INDUSTRIES P.L.C.

British Appl. 2,135,669A

A Pt cathode and Pt or TiO₂/RuO₂ anode may be employed in the production of tetrafluoroethylene by the electrolytic reduction of an electrolyte solution containing dichlorodifluoromethane.