

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Optical Behavior of Sputter-Deposited Platinum-Oxide Films

C. R. AITA, *J. Appl. Phys.*, 1985, 58, (8), 3169-3173

A series of Pt-O alloys were grown by reactive sputter deposition on water-cooled Si and glass substrates. Optical behaviour in the near u.v.-visible and near i.r. regions was studied by spectrophotometry. Changes in reflection and transmission behaviour were correlated with changes in film chemistry and structure, especially oxide formation and loss of long-range crystallographic order.

Pt-Co Magnets Produced by DC Triode Sputtering

E. W. HILL, G. R. HOFFMAN and A. M. MCCULLOUGH, *J. Phys. (Paris), Colloq. No. 6*, C6-291-C6-294

Thin permanent magnetic films of equiatomic PtCo have been produced by DC triode sputtering. Films up to 6 μ m thick have been deposited onto sapphire substrates and give (BH)_{max} products of 72kJ/m³ when optimally heat treated.

Shape Memory Effect in an Ordered Fe₃Pt Alloy Associated with the FCC-FCT Thermoelastic Martensite Transformation

R. OSHIMA, S. SUGIMOTO, M. SUGIYAMA, T. HAMADA and F. E. FUJITA, *Trans. Jpn. Inst. Met.*, 1985, 26, (7), 523-524

The shape memory effect in an ordered Fe-24.9 at.%Pt alloy associated with a f.c.c.-f.c.t. thermoelastic martensitic transformation was examined. The Fe₃Pt alloy was manufactured and electrical resistance/temperature curves at different transformation temperatures were plotted. Fe₃Pt (M_s < 77K) with order parameter, S=0.78, has a martensitic transformation independent of the f.c.c.-b.c.t. or f.c.c.-b.c.c. transformation and is associated with a remarkable shape memory effect.

Magnetic and Superconducting Properties of UPt₃

J. J. M. FRANSE, A. DE VISSER, A. MENOVSKY and P. H. FRINGS, *J. Magn. & Magn. Mater.*, 1985, 52, (1-4), 61-69

Results of experimental studies on the thermodynamic and transport properties of the heavy fermion superconductor UPt₃ are reviewed. The studies include high magnetic field and high pressure experiments in the normal and superconducting states and alloying effects on the normal and superconducting state properties.

A New One-Dimensional Long Period Superstructure in Pd₃Ce

N. KUWANO, S. HIGO, K. YAMAMOTO, K. OKI and T. EGUCHI, *Jpn. J. Appl. Phys. Lett.*, 1985, 24, (8), L663-L665

An ingot of Pd-Ce containing about 17at.%Ce was prepared and its structure analysed by X-ray diffraction and electron microscopy. Pd₃Ce has two phases, one stable at low temperature and the other stable at high temperature.

The Au-Pd (Gold-Palladium) System

H. OKAMOTO and T. B. MASSALSKI, *Bull. Alloy Phase Diagrams*, 1985, 6, (3), 229-235, 283

An assessed Au-Pd phase diagram for 0-1600°C which includes a liquid phase is presented and backed by several references. Liquidus and solidus temperatures are given for various compositions. Long range order for Au₃Pd, AuPd, and AuPd is discussed, as is short range order.

Hydrogen in Deformed and Amorphous Pd₈₀Si₂₀ Compared to Hydrogen in Deformed and Crystalline Palladium

R. KIRCHHEIM, A. SZÖKEFALVI-NAGY, U. STOLZ and A. SPEITLING, *Scr. Metall.*, 1985, 19, (7), 843-846

H₂ diffusivity, e.m.f. and resistivity increments in amorphous Pd₈₀Si₂₀ before and after cold rolling were measured and compared with the corresponding quantities in crystalline Pd. Amorphous Pd₈₀Si₂₀ samples show a different concentration dependence compared to crystalline Pd.

Effects of Implanted Hydrogen on Pd₂Si Formation

A. PACCAGNELLA, G. MAJNI, G. OTTAVIANI and G. DELLA MEA, *Appl. Phys. Lett.*, 1985, 47, (8), 806-808

Preliminary results on Pd₂Si formation in the presence of H implanted in a (III) Si substrate near the Pd/Si interface after Pd deposition are reported. The implantation energy was chosen so that most of the H atoms stopped near the Pd/Si interface. Changes in H distribution in annealed samples were investigated.

Electrical Resistivities of Iridium, Palladium, Rhodium and Tungsten at Temperatures between 295 and 1100K

E. Y. GARCIA and D. G. LÖFFLER, *J. Chem. Eng. Data*, 1985, 30, (3), 304-305

Using thin wire samples, the relationships between electrical resistance and temperature have been established for Pd, Rh, Ir and W in the range 295 to 1100K. A polynomial expression is given which fits these and other data with <1% deviations. The electrical resistivity of Ir at 295K is given as 9.01 $\mu\Omega$ cm.

Adsorption and Desorption of NO from Rh{111} and Rh{331} Surfaces

L. A. DELOUISE and N. WINOGRAD, *Surf. Sci.*, 1985, **159**, (1), 199-213

The adsorption and desorption of NO on clean Rh{111} and Rh{331} single crystal surfaces was followed by various techniques. At saturation coverage there was ~10 times more dissociated species on the Rh{331} surface at 300K than on the Rh{111} surface. The molecular states of NO_{ads} were β_1 and β_2 , which possess different chemical reactivity, and are present in different proportions on the two surfaces. The populations are coverage and temperature dependent.

Growth of a Bicrystal Superlattice: Ru-Ir

J. E. CUNNINGHAM and C. P. FLYNN, *J. Phys. F*, 1985, **15**, (9), L221-L226

The growth of a high quality bicrystal superlattice formed from alternating layers of h.c.p. Ru and f.c.c. Ir metals is reported. Ir layers, which are thick compared with the Ru do grow in the f.c.c. structure, whereas thin Ir layers take the h.c.p. structure, probably due to strain effects.

Lifetimes of the Lowest Excited State of Tris(2,2'-Bipyridine)Ruthenium(II) and Its Amphipathic Derivative in Micellar Systems

Y. KAIZU, H. OHTA, K. KOBAYASHI, H. KOBAYASHI, K. TAKUMA and T. MATSUO, *J. Photochem.*, 1985, **80**, (1), 93-103

The luminescence decay lifetimes of ([Ru(bpy)₃]²⁺) and its amphipathic derivative ([RuC₁₂B]²⁺) were measured in H₂O, D₂O, CH₃OH, CD₃OH and CH₃OD solutions, as well as in micellar solutions of Na dodecylsulphate in H₂O and D₂O. They reveal the role of the protic solvent molecules in the deactivation of the excited Ru(II) complexes. The lifetimes of the complexes reduce with increasing size of the waterpool in the inverted micellar solution. ([Ru(bpy)₃]²⁺) is present in the waterpool, but ([RuC₁₂B]²⁺) is buried inside the anionic interface with its aliphatic sidechains penetrating deep into the hydrophobic domain.

CHEMICAL COMPOUNDS

The Preparation and Properties of Compounds Containing Pt(III)

J. D. WOOLLINS and P. F. KELLY, *Coord. Chem. Rev.*, 1985, **65**, 115-140

Information on compounds with an average Pt oxidation number of (III) is presented. The material is divided into mixed valance Pt(III)-Pt(IV) systems, binuclear compounds, such as sulphate-, phosphate-, hydroxide-, peroxide- and carboxylate-bridged species and Pt blues and related systems, which include binuclear compounds containing biologically relevant ligands. (108 Refs.)

Synthesis and Structure of the [Ni₃₈Pt₆-(CO)₄₈H_{6-n}]ⁿ⁻ (n=5,4) Ions: Ni-Pt Clusters as Models for "Chemistry" Crystallites

A. CERIOTTI, F. DEMARTIN, G. LONGONI, M. MANASSERO, M. MARCHIONNA, G. PIVA and M. SANSONI, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, (8), 697-698

The syntheses and structures of a series of title clusters is discussed. These compounds have been isolated in a crystalline form and two of the structures have been determined by XRD. They constitute the highest nuclearity carbonyl clusters fully characterized, so far. Preliminary measurements suggest unusual magnetic behaviour.

Homoleptic Isocyanide Complexes of Ruthenium(II) and Osmium(II)

S. M. TETRICK and R. A. WALTON, *Inorg. Chem.*, 1985, **24**, (21), 3363-3366

A first general synthetic route to the homoleptic metal (II) complexes [M(CNR)₆](PF₆)₂ M=Ru or Os is reported. The complexes are made by reaction of di-Ru(II, III) and di-Os(III) acetates Ru₂(O₂C-CH₃)₄Cl and Os₂(O₂CCH₃)₄Cl₂ with alkyl isocyanides, RNC (R=CHMe₂, CMe₃, or C₆H₁₁).

ELECTROCHEMISTRY

Square Wave Voltammetry on Platinum Microdisk Electrodes Using Synchronous Remodulation

S. A. SCHUETTE and R. L. MCCREERY, *J. Electroanal. Chem. Interfacial Electrochem.*, 1985, **191**, (2), 329-342

Pt microdisk electrodes were manufactured and used in one form of square wave voltammetry for analytical measurements. The benefits of using microdisk electrodes are examined, as is the square wave voltammetry used. A detection limit of $2 \times 10^{-7} M$ was obtained for ferrocene in acetonitrile. The rapid charging current decay allows the use of high modulation frequencies and fast voltammetric scans.

Electrochemical Permeability Control through a Bilayer-Immobilized Film Containing Redox Sites

Y. OKAHATA, G.-I. ENNA, K. TAGUCHI and T. SEKI, *J. Am. Chem. Soc.*, 1985, **107**, (18), 5300-5301

The reversible permeability control through a viologen (4,4'-bipyridinium)-containing bilayer-film deposited on a Pt minigrad sheet by electrochemical redox reaction is reported. The Pt minigrad was supported on a polyethylene tube. With different potentials varying from -0.50V vs. SCE to 0V permeability changes occurred, and could be reproduced repeatedly. The changes may be attributed to the fluidity change of the bilayer film on the Pt grid because of the T_c transitions of bilayers by redox reactions.

Effect of Platinisation on the Electrochemical Behavior of the TiO₂ Electrode in Aqueous Solutions

K. UOSAKI, R. YONEDA and H. KITA, *J. Phys. Chem.*, 1985, **89**, (19), 4042-4046

The electrochemical behaviour of platinised TiO₂ electrodes was investigated and was found to increase the H₂ evolution reaction rate but not to affect the kinetics of O₂ evolution at TiO₂ single-crystal electrodes. At polycrystalline TiO₂ electrodes H₂ evolution and O₂ evolution were accelerated by platinisation.

Electrocatalytic Reduction of CO₂ at a Chemically Modified Electrode

T. R. O'TOOLE, L. D. MARGERUM, T. D. WESTMORELAND, W. J. VINING, R. W. MURRAY and T. J. MEYER, *J. Chem. Soc., Chem. Commun.*, 1985, (20), 1416-1417

Electropolymerised complex Re(4-vinyl-4¹-methyl-2,2¹-bipyridine)(CO)₃Cl as a polymeric film on a Pt electrode, electrocatalytically reduces CO₂ to CO with turnover numbers greatly exceeding those observed for the analogous electrocatalytic reduction of CO₂ by Re(bpy)(CO)₃Cl on Pt gauze electrode.

Removal of Colloidal Silicon in Simulated Seawater by a Dynamic Multi-Short-Circuited Galvanic Cell

J.-E. OSTERHOLM, P. W. KRAMER and H. K. YASUDA, *Ind. Eng. Chem., Prod. Res. Dev.*, 1985, **24**, (3), 468-473

An inexpensive dynamic multi-short-circuited galvanic cell with Pt-Al electrodes was used to study the removal of colloidal SiO₂ from seawater, as a pretreatment step for the desalination of seawater by reverse osmosis. The rate of SiO₂ removal was affected by the flowrate of the solution through the cell, the dissolved O content of the solution, the nature of the Al electrode surface and the number of contact points between the Al and Pt. The SiO₂ content was reduced by 95% by this cell. The Pt is not consumed, but the Al is, and a module made of Pt with replaceable Al is suggested as a first step in purifying brackish water or seawater.

Clay Modified Electrodes. Electrochemical and Electron Spin Resonance Studies of Montmorillonite Layers

D. EGE, P. K. GHOSH, J. R. WHITE, J.-F. EQUEY and A. J. BARD, *J. Am. Chem. Soc.*, 1985, **107**, (20), 5644-5652

Montmorillonite films (30nm-3μm thick) with and without added poly(vinylalcohol) were cast onto Pt, glassy C and SnO₂/glass and used as electrodes. The electrochemistry of cationic species incorporated in the films, Ru(bpy)₃²⁺, Os(bpy)₃²⁺ and Fe(bpy)₃²⁺ is described. The effective diffusion coefficients of the Os and Fe species in these films were ~ 10⁻¹² cm²/s.

The Direct Electrochemistry of Redox Proteins at Metal Oxide Electrodes

M. A. HARMER and H. A. O. HILL, *J. Electroanal. Chem. Interfacial Electrochem.*, 1985, **189**, (2), 229-246

The DC cyclic voltammetry of several redox proteins at thin film RuO₂ electrodes is described. Responses on varying pH and solution ionic strengths were observed. The results highlight the importance of electrostatics at the electrode/solution interface. Preliminary results using IrO₂, Na_{0.7}WO₃ and single crystal RuO₂ electrodes are reported. Subtle differences in behaviour are found at single crystal and thin film RuO₂ electrodes.

PHOTOCONVERSION

Rate Enhancement of Photooxidation of CN⁻ with TiO₂ Particles

T. L. ROSE and C. NANJUNDIAH, *J. Phys. Chem.*, 1985, **89**, (17), 3766-3771

The rate of photooxidation of CN⁻ by platinised anatase particles was investigated as a function of particle size, platinisation and pH. The reaction rate constants increased on increasing the surface area of the particles, platinising the TiO₂ and lowering the pH from 14 to 11. The fastest rate constant was >500 times faster than any previously reported.

Photochemical Water Cleavage in Suspensions in Pt-Loaded Titania Particles with 0.7% Overall Light to Chemical Conversion Efficiency

B. GU, J. KIWI and M. GRÄTZEL, *Nouv. J. Chim.*, 1985, **9**, (8/9), 539-543

Band gap irradiation of alkaline aqueous TiO₂ suspensions loaded with ultrafine Pt particles via ion exchange with Pt(NH₃)₄²⁺, and subsequent reduction, produces H₂ with an overall light to chemical conversion efficiency of 0.1%. The anodic reaction is H₂O oxidation to peroxide. Addition of Ba²⁺ ion to the suspension increases the overall conversion to 0.7% and the Ba²⁺ also drastically decreases the rate of recombination of H₂ with O₂ and that for the photo-uptake of O₂. Cyclic performance is achieved by decomposing the peroxide at 200-300°C.

Photoelectrochemical Measurements on Thermally Grown Platinum Containing Iron Oxide Photoanodes

M. R. ST. JOHN, A. J. TILLER, R. L. COOK and A. F. SAMMELLS, *J. Electrochem. Soc.*, 1985, **132**, (8), 1859-1864

Pt was found to be an effective electrocatalyst when incorporated into the bulk of thermally grown α-Fe₂O₃ during its preparation. When the α-Fe₂O₃ was used as photoanodes for the photodecomposition of alkaline aqueous solutions into H₂ and O₂, the addition of Pt increased the carrier density and gave a more negative flatband potential.

Photoactivated Oxidation of Alcohols by Oxygen

R. E. CAMERON and A. B. BOCARSLY, *J. Am. Chem. Soc.*, 1985, **107**, (21), 6116-6117

Primary and secondary alcohols can be converted to the corresponding aldehyde or ketone by using O₂ and visible light. The process is catalysed by the presence of H₂, PtCl₆ and CuCl₂. The reaction occurs at room temperature and 1 atm O₂ in neat alcohol. The catalytic cycle is stable for several days when using primary or secondary substrate alcohols.

In Situ Generation of Catalyst-Coated CdS Particles in Polymerized and Unpolymerized Surfactant Vesicles and Their Utilization for Efficient Visible-Light-Induced Hydrogen Production

Y.-M. TRICOT, R. EMEREN and J. H. FENDLER, *J. Phys. Chem.*, 1985, **89**, (22), 4721-4726

Colloidal CdS particles were in situ generated and coated by Rh or Pt in vesicles formed from dihexadecyl phosphate, (DHP), dioctadecyldimethylammonium chloride, and from a surfactant containing a polymerisable styrene moiety (A). A clearly detectable fluorescence emission was found only for CdS in DHP vesicles. Photosensitised H₂ generation by visible light was measured and electron donors were tested. EDTA was efficient in polymerised (A) vesicles. Benzyl alcohol was a very efficient electron donor in cationic vesicle systems, but not in negatively charged systems. With 1% benzyl alcohol at 40°C in vesicles prepared from polymerised (A), a maximum rate of ~200 μmol/h of H₂ was achieved, using only 0.82 mg CdS/Rh catalyst. The overall quantum yield of H₂ generated at 400 nm was 10%.

Characteristics of Photoelectrochemical Cells with Iron-Oxide/n-Si Heterojunction Photoanodes

T. OSAKA, N. HIROTA, T. HAYASHI and S. S. ESKILOSEN, *Electrochim. Acta*, 1985, **30**, (9), 1209-1212

The Fe oxide/n-Si heterojunction electrode was studied as a photoanode for a regenerative photoelectrochemical (PEC) cell. Modifying the top layer of the electrode with Pd or RuO₂ enhanced the optical-to-electrical conversion efficiency. A stable PEC had conversion efficiencies of 1.34% and 1.60% for a Pd- and a RuO₂-modified electrode, respectively.

Preparation of Active CdS/RuO_x Particles for the Photogeneration of H₂

D. H. M. W. THEWISSEN, K. TIMMER, E. A. VAN DER ZOUWEN-ASSINK, A. H. A. TINNEMANS and A. MACKOR, *J. Chem. Soc., Chem. Commun.*, 1985, (21), 1485-1487

The preparation of RuO_x from RuO₄ and in situ generated Ru hydroxide or ruthenate ions, followed by calcination at 400°C gives active catalysts without noxious oxidation of the CdS support. The nature and activity for the photogeneration of H₂ by various CdS/RuO_x powders are given.

Photoelectrochemical Behaviour of RuS₂ Semiconducting Electrodes

A. M. REDON, *Solar Cells*, 1985, **15**, (1), 27-37

Various parameters of sintered and single crystal RuS₂ photoelectrodes are examined. Estimated band gap values for the sintered electrode were 1.5 eV for the direct transition, 1.8 eV for the indirect transition and 2.3 eV for the single crystal. RuS₂ appears to be a good semiconductor for O₂ evolution and solar energy conversion due to its great stability. The shape and time evolution of the photocurrent are examined.

Quantum Yield of Formation of Methylviologen Radical Cation from the Photolysis of the Ru(bpz)₃²⁺/Methylviologen/EDTA System

D. R. PRASAD, D. HESSLER and M. Z. HOFFMAN, *Chem. Phys. Lett.*, 1985, **121**, (1, 2), 61-64

Values for the quantum yield of formation of MV^{•+} as a function of pH, [MV²⁺] and [EDTA] are given, and Ru(bpz)₃²⁺/MV²⁺/EDTA is evaluated as a model system for the photochemical storage of radiant energy, since it has been suggested that Ru(bpz)₃²⁺ is a superior catalyst to Ru(bpy)₃²⁺ for water splitting reactions.

ELECTRODEPOSITION AND SURFACE COATINGS

Pt-Al₂O₃ Selective Cermet Coatings on Superalloy Substrates for Photothermal Conversion up to 600°C

TRAN KHANH VIEN, C. SELLA, J. LAFAIT and S. BERTHIER, *Thin Solid Films*, 1985, **126**, (1/2), 17-22

Pt-Al₂O₃ cermet coatings deposited by r.f. cosputtering on stainless steel and superalloy substances were manufactured and tested. Optical properties were measured before and after annealing procedures and optimisation of the absorber selectivity was attempted. The cermet proved to be a good coating for high temperature photothermal selective absorbers and selectivity could be improved. High temperature selective absorbers for industrial applications can therefore be made.

Plating Process for the High Speed Deposition of Palladium for Contact Devices

J. VANHUMBEECK, *Siemens Forsch.-Entwicklungsber.*, 1985, **14**, (3), 140-146

A new high speed Pd plating process with an electrolyte of Pd chloride, using NH₃ as complexing agent and phosphate as buffer is described. The current density and electrolyte movement determine operating conditions to give smooth, semi-bright, crackfree deposits. The contact resistance of the deposits are low and stable even after corrosion testing. Pd layers with an upper Au flash have good wear resistance and a low coefficient of friction.

Electrodeposition of Palladium-Nickel Coatings from a Hydrochloric Acid Electrolyte

I. P. NENOV and L. TEBAL, *Metalloberflaeche*, 1985, **39**, (11), 405-410

A new HCl electrolyte for electrodeposition of Pd-Ni alloy coatings has been developed. The pH of the electrolyte for optimum conditions is 4.5. The thickness of the deposit, temperature of the solution and current density for deposition are discussed. The electrolyte has a simple synthesis and besides the salts of both metals and the organic ligands contains no other additions.

Electrodeposition of Ruthenium from a LiCl-KCl Melt

A BETTELHEIM, F. BROITMAN, U. MOR and R. HARTH, *J. Electrochem. Soc.*, 1985, **132**, (7), 1775-1776

Thick adherent and compact electrodeposits of Ru were obtained from a LiCl-KCl melt at temperatures as low as 400°C, provided that the melt was saturated with HCl. Coatings up to 4.4µm thick, with a cathodic current efficiency of 77% were produced in a bath containing a Ru ion concentration of 0.26 w/o on applying a current density of 5.4mA/cm².

LABORATORY APPARATUS AND TECHNIQUE

New Platinum Silicide Formation Method Using Reaction between Platinum and Silane

Y. TAKAHASHI, H. ISHII and J. MUROTA, *J. Appl. Phys.*, 1985, **58**, (8), 3190-3194

A new method for the formation of Pt silicide is proposed. Pt film reacts with SiH₄ at 250-400°C forming Pt silicide. This formation with SiH₄ is less influenced by O contamination than the reaction between Pt and substrate Si. Pt silicide formation was not influenced by Si-Pt interface contamination, and erosion of Si from the substrate can be reduced without limiting Pt silicide thickness, since Si used for the silicide formation comes from SiH₄. Thus this Pt silicide will be useful for the contact electrode on shallow diffused layer of fine pattern Si integrated circuits and for gate and interconnect metallisations.

Performance of Carbon Monoxide-Sensitive MOSFET's with Metal-Oxide Semiconductor Gates

K. DOBOS and G. ZIMMER, *IEEE Trans. Electron Devices*, 1985, **32**, (7), 1165-1169

A multilayer PdO-Pd gate metallisation was investigated as a MOS-CO sensor. The sensor had high sensitivity to CO and good electrical control of the transistor. By comparison with a SnO₂ commercial CO sensor it has lower cross sensitivity for CH₄, butane and C₂H₅OH. The MOSFET was less influenced by humidity than the commercial sensor.

MOS Hydrogen Sensors with Ultrathin Layers of Palladium

G. J. MACLAY, *IEEE Trans. Electron Devices*, 1985, **32**, (7), 1158-1164

MOS gas sensors were fabricated on n- and p-type Si(5-7Ωcm) with thermal oxide layers from 66-269Å thick. A 30Å Pd layer was deposited through an evaporation melt and covered by a 350 Å thick Au layer. The devices were sensitive to H₂ at room temperature. They also had faster response and recovery at room temperature, and reduced magnitude of response than ones with a 300Å thick Pd layer. Devices on p-Si were faster than on n-Si.

HETEROGENEOUS CATALYSIS

Effect of Pellet Mobility on the Poisoning Behavior of Packed-Bed Catalytic Converters

B. K. CHO and S. H. OH, *Ind. Eng. Chem., Process Des. Dev.*, 1985, **24**, (4), 897-906

A unique method for analysing the effect of pellet mobility on the poisoning behaviour of packed-bed catalytic converters under pore-mouth poisoning conditions is used to examine the oxidation of CO, C₂H₆, CH₄ and H₂ over Pt/Al₂O₃. Warm up times and steady-state conversions could be simultaneously examined, and the effects of several variables are examined. A single-compartment converter provides the best overall performance, and catalysts with large effective diffusivity have smaller performance deterioration than those with small effective diffusivity, also an increase in impregnation depth up to 200-300µm would improve warm up performance without affecting the warmed up performance.

Oxidation of Tritium in Packed Bed of Noble Metal Catalyst for Detritiation from System Gases

M. NISHIKAWA, T. TAKEISHI, K. MUNAKATA, K. KOTOH and M. ENOEDA, *J. Nucl. Mater.*, 1985, **135**, (1), 1-10

Catalytic oxidation rates of tritium over the catalyst beds Pt/Al₂O₃ or Pd/Al₂O₃ are discussed. These catalysts give effective oxidation rates of tritium in the ambient temperature range. The adsorption performance of tritiated water in the catalyst bed is also discussed.

Oxidation of Ethanol on Silica Supported Noble Metal and Bimetallic Catalysts

R. D. GONZALEZ and M. NAGAI, *Appl. Catal.*, 1985, **18**, (1), 57-70

The oxidation of C₂H₅OH was studied over SiO₂ supported Pt, Ru, Pt-Ru, Pd and Rh catalysts. Pt was the most active catalyst for CO₂ formation. Ru was highly selective for acetaldehyde formation at 40-100°C. Infrared studies suggest the presence of an acetate intermediate in addition to an adsorbed ethoxy species and chemisorbed CO. The ethoxy species are adsorbed both on Pt and SiO₂.

Dynamic Behaviour of Automotive Catalysts. 4. Impact of Air/Fuel Ratio Excursions during Driving

R. K. HERZ and E. J. SHINOUSKIS, *Ind. Eng. Chem., Prod. Res. Dev.*, 1985, **24**, (3), 385-390

The analyses of emissions from automobiles over Pt/Pd/Rh/Al₂O₃ and Pt/Pd/Rh/Ce/Al₂O₃ catalysts during the warmed up portion of the Federal test procedure are compared. The O storage capacity obtained by adding Ce to the catalysts gave dramatically increased CO conversion following lean-to-rich step changes. Near lean A/F ratios, near the stoichiometric point, and during the as cycled A/F tests the two catalysts were in reasonably good agreement. It is concluded that large amplitude low frequency components of A/F fluctuations must be considered in future studies.

A Prototype Truck Powered by Hydrogen from Organic Liquid Hydrides

M. TAUBE, D. RIPPIN, W. KNECHT, D. HAKIMFARD, B. MILISAVLJEVIC and N. GRUENENFELDER, *Int. J. Hydrogen Energy*, 1985, **10**, (9), 595-599

A prototype truck has been constructed to use a H₂-burning engine with H₂ injection under 10 bar pressure. The engine efficiency is ~32%, with exhaust gas temperature of ~700°C and power of ~150 kW. The H₂ at 10 bar is produced continuously by catalytic splitting of methylcyclohexane on 0.25Pt-0.25Re/Al₂O₃ on board the truck. The reaction occurred at 10 bar pressure, 400°C, efficiency ~0.80 and lifetime several hundred hours, without H₂ recycling.

Behaviour of Hydrogenation Catalysts. 1. Hydrogenation of Soybean Oil with Palladium

J. D. RAY, *J. Am. Oil Chem. Soc.*, 1985, **62**, (8), 1213-1217

A statistical method for evaluating catalysts was used in determining the behaviour of 5% Pd/C catalysts for soybean oil hydrogenation. Pd had very high activity, but offered no special advantage in trans-isomer formation or selectivity. Pd could substitute for Ni catalysts at greatly reduced temperature and catalyst concentration, for production of salad oil or margarine basestock from soybean oil.

Water Production on Palladium in Hydrogen-Oxygen Atmospheres

L.-G. PETERSSON, H. M. DANNETUN and I. LUNDSTRÖM, *Surf. Sci.*, 1985, **163**, (1), 273-284

Water production on a Pd-SiO₂-Si structure in various O₂-H₂ atmospheres was measured together with work function, photoelectron spectroscopies and H sensitive measurements. A critical O₂:H₂ pressure ratio is confirmed, above which water production rate decreases with increasing O₂ pressure, and increases with increasing H₂ pressure. Below the critical ratio the H₂O production rate is proportional to O₂ pressure and independent of H₂ pressure.

Methanol and Methane Formation over Palladium/Rare Earth Oxide Catalysts

C. SUDHAKAR and M. A. VANNICE, *J. Catal.*, 1985, **95**, (1), 227-247

Lanthanide rare earth oxide supports for Pd systems provide very good CO hydrogenation catalysts, especially for CH₃OH formation. At low temperatures and 1 atm pressure the major product was CH₃OH, but selectivity shifted to CH₄ at higher temperatures. Turnover frequency values for CH₃OH varied more than tenfold, and all catalysts except Pd/Eu₂O₃ had an order of magnitude higher activity than on Pd/SiO₂ or pure Pd metal. Activation energies for CH₃OH were consistently around 32 kcal/mole. Pd/La₂O₃ and Pd/Nd₂O₃ were the most active CH₃OH catalysts, and Pd/CeO₂ was the least active. (44 Refs.)

Polybenzimidazole-Supported Heterogeneous Palladium Catalysts

N.-H. LI and J. M. J. FRÉCHET, *J. Chem. Soc., Chem. Commun.*, 1985, **16**, (16), 1100-1101

The polybenzimidazole-PdCl₂ was prepared easily and the loading of PdCl₂ onto the PBI could be readily controlled by varying the Pd:PBI ratio. The catalyst with only Pd⁰ was extremely stable, and could be heated to 300°C for several hours without decomposition, and showed excellent activity in reducing various nitro compounds. The catalyst was easy to recycle and showed no loss of activity or Pd content after more than 20 cycles, or after heating in air to 300°C for 6h.

The Oxidation of Carbon Monoxide on Polycrystalline Rhodium under Knudsen Conditions. I. Reaction with Oxygen. II. Reaction with Nitrogen Monoxide. III. Simultaneous Reaction with Oxygen and Nitrogen Monoxide

H.-G. LINTZ and T. WEISKER, *Appl. Surf. Sci.*, 1985, **24**, (2), 251-258; 259-267; 268-273

The reaction between O₂ and CO on polycrystalline Rh ribbon was observed at 300-1100K and pressures between 10⁻⁵ and 10⁻⁴ torr. The reaction on Rh has similar features to that on Pt. The reaction between CO and NO on polycrystalline Rh ribbon was also observed. In the temperature range 300-1000K the partial pressures of the two reactants varied 0.1 < p_{NO}/p_{CO} < 100 at pressures 10⁻⁴-10⁻⁵ torr in the reactor. The CO oxidation using mixtures of O₂ and NO was studied. At high temperatures the amount of NO reduced is directly proportional to its fraction in the oxidising gas. At low temperatures NO may be reduced with high selectivity.

Surface Conversion of Benzene to Acetylene

W. L. PARKER, R. M. HEXTER and A. R. SIEDLE, *J. Am. Chem. Soc.*, 1985, **107**, (15), 4584-4585

Using a 10% Rh/α-Al₂O₃ catalyst, benzene was converted to acetylene under UHV conditions.

Selective Synthesis of Ethanol over Rh-Ti-Fe-Ir/SiO₂ Catalyst and High Pressure Syngas Conversion

H. ARAKAWA, T. FUKUSHIMA, M. ICHIKAWA, S. NATSUSHITA, K. TAKEUCHI, T. MATSUZAKI and Y. SUGI, *Chem. Lett. Jpn.*, 1985, (7), 881-884

A high performance Rh-Ti-Fe-Ir/SiO₂ catalyst for ethanol production has been developed. Ethanol was produced with > 50% selectivity from syngas at 50 atm and 260°C.

Postcrosslinking of Rhodium Catalysts Bound to Polyacrylic Acid: A Useful Technique to Enhance and Preserve Catalytic Activity

G. VALENTINI, G. SBRANA, G. BRACA and P. DA PRATO, *J. Catal.*, 1985, 96, (1), 41-50

A significant improvement in catalytic performance of triphenylphosphine polyacrylate Rh(I) complexes was obtained on optimising the preparation conditions and by adding a crosslinking agent (hexamethylenediamine). The crosslinked systems, insoluble in organic solvents, were obtained in high yields and had catalytic activity for pent-1-ene hydrogenation and isomerisation higher than that of a low molecular weight analog working in solution. The systems had remarkable catalytic stability and very constant selectivity upon recycling.

Water Gas Shift Reaction Catalyzed by Osmium Compounds Supported on Zeolites. Evidences for Formation in the Presence of a Base of a Trapped Hydrido-Carbonyl Catalyst

M. LENARDA, R. GANZERIA, M. GRAZIANI and R. SPOLIARICH, *J. Organomet. Chem.*, 1985, 290, (2), 213-218

Thermal treatment of Os₃(CO)₁₂/zeolite gives a new species which in the presence of base is an active catalyst for the water gas shift reaction. When NaOH is used the hydrido-carbonyl anion [H₃Os₃(CO)₁₀]⁻ is formed and trapped in the zeolite framework. This compound is also an active catalyst for the water gas shift reaction.

Effect of Potassium and Phosphorus on the Hydrogenation of CO over Alumina-Supported Ruthenium Catalyst

T. OKUHARA, H. TAMURA and M. MISONO, *J. Catal.*, 1985, 95, (1), 41-48

The effects of additives K, B and P on Ru/Al₂O₃ were investigated for the adsorption and catalytic hydrogenation of CO. Addition of K increased the strength of CO adsorption by enhancing the back donation from Ru to CO. K also significantly increased the olefin:paraffin ratios in product hydrocarbons and suppressed CH₄ formation, while catalytic activity was decreased by the addition. Addition of P or B brought about opposite changes in both CO adsorption and CO hydrogenation.

Metal Cluster Catalysis: Preparation and Catalytic Properties of Anionic Triruthenium Clusters Anchored to Functionalized Silica

Y. DOI, H. MIYAKE, A. YOKOTA and K. SOGA, *Inorg. Chim. Acta*, 1985, 105, (1), 69-73

The anionic cluster [Ru₃H(CO)₁₁]⁻ was anchored onto a SiO₂ surface, modified with ammonium and pyridinium functions and used as a catalyst for the water gas shift reaction and for ethylene and CO hydrogenations. The SiO₂ anchored clusters were stable up to 150°C and exhibited higher catalytic activities for C₂H₄ hydrogenation (70°C) and the water gas shift reaction (150°C) than those of SiO₂ anchored Na[Ru₃H(CO)₁₁].

HOMOGENEOUS CATALYSIS

Catalytic Properties of the Platinum and Palladium Blacks Obtained from Vaporized Metals as Revealed in the Hydrogenation of 4-Methylcyclohexanone in Ethanol

S. NISHIMURA, S.-I. IWAFUNE, T. NAGURA, Y. AKIMOTO and M. UDA, *Chem. Lett. Jpn.*, 1985, (8), 1275-1278

Pt and Pd blacks were obtained from vapourised metals and catalysed the formation of acetal efficiently during the hydrogenation of 4-methylcyclohexanone in ethanol. Pt(NRIM) was the most active of the Pt blacks investigated, and had a much smaller surface area than the others.

Colloidal Platinum Catalysts Prepared by Hydrogen- and Photo-Reduction in the Presence of Surfactant

N. TOSHIMA, T. TAKAHASHI and H. HIRAI, *Chem. Lett. Jpn.*, 1985, (8), 1245-1248

Chloroplatinic acid in an aqueous solution was reduced by H₂ molecules or photo irradiation in the presence of surfactants to produce colloidal dispersions of Pt protected by the surfactants. Particles produced by photoreduction were smaller and more narrowly dispersed than those prepared by H₂ reduction. They were highly active catalysts for olefin hydrogenation.

Stability of the Structure of Polynuclear Cluster Compounds and Their Reaction Activity for Olefin Hydroformylation

W.-J. XIE, F.-Y. JIAO, S.-K. YANG, Y.-Q. YIN and D.-G. LI, *J. Catal. (Dalian, China)*, 1985, 6, (2), 172-178

RhCl₃·3H₂O was used as starting material for the synthesis of Rh₄(CO)₁₂ and Rh₆(CO)₁₆. These two polynuclear clusters were very good catalysts for the hydroformylation of olefins, such as hexene-1, heptene-1 and cyclohexene. The catalytic activities for hexene-1 hydroformylation of these two Rh clusters were compared to those of RhCl(CO)(PPh₃)₂, RhCo₃(CO)₁₁ and ClCo₃(CO)₉.

Synergistic Behavior of Homogeneous Ruthenium-Rhodium Catalysts for Hydrogenation of Carbon Monoxide

B. D. DOMBEK, *Organometallics*, 1985, 4, (10), 1707-1712

Homogeneous solutions containing complexes of both Ru and Rh exhibit good selectivity for the catalytic hydrogenation of CO to ethylene glycol. Reactions were studied at pressures from 400-850 atm and 190-240°C. Iodide ion was an effective promoter. Metal complexes observed in solutions included $[\text{HRu}_3(\text{CO})_{11}]^-$, $[\text{Ru}(\text{CO})_3\text{I}_3]^-$ and $[\text{Rh}(\text{CO})_2\text{I}_2]^-$.

Water Gas Shift Reaction, Development and Study of Efficient Homogeneous Catalysts Based on Iridium-Diimine Complexes

J. P. COLLIN, R. RUPPERT and J. P. SAUVAGE, *Nouv. J. Chim.*, 1985, 9, (6), 395-404

A detailed study of the water gas shift reaction catalysed by several Ir (I) complexes under a range of experimental conditions is presented. The most efficient catalytic system was obtained from Ir(dmp-S)(COD)⁺ (dmp-S=sulphonated derivative of 2,9-dimethyl 1,10-phenanthroline; COD=1,5-cyclooctadiene). Turnover frequencies close to 10⁷/h have been observed at 100°C and under 1atm CO, making this system one of the most efficient catalysts ever reported. The chemical stability of the homogeneous catalyst is good, even after several thousand cycles; and activity remains unchanged. (85 Refs.)

The Chemistry and Catalytic Properties of Ruthenium and Osmium Complexes. Part 1. Homogeneous Catalysis of Organic Reactions by Bromo(carbonyl)hydridotris(triphenylphosphine)osmium(II)

R. A. SÁNCHEZ-DELGADO, A. ANDRIOLLO, E. GONZÁLEZ, N. VALENCIA, V. LEÓN and J. ESPIDEL, *J. Chem. Soc., Dalton Trans.*, 1985, (9), 1859-1863

The complex $[\text{OsH}(\text{Br})(\text{CO})(\text{PPh}_3)_3]$ catalyses C=C bond migration, isomerisation of allyl alcohol, hydrogenation of acyclic and cyclic olefins, dienes, acetylenes, aldehydes, ketones, α , β -unsaturated aldehydes and ketones, and hydroformylation of alkenes under moderate reaction conditions. This catalyst combines high activity and selectivity under mild conditions with ease of preparation, handling and recycling.

The Generation of N-Alkylformamides from Synthesis Gas and Ammonia

J. F. KNIFTON, *J. Chem. Soc., Chem. Commun.*, 1985, (20), 1412-1414

N, N-dimethylformamide and N-methylformamide have been prepared from syngas with NH₃ by Ru melt catalysis. Several different catalyst precursors were used, but mostly employing Ru₃(CO)₁₂.

(Cyclopentadienone) Ruthenium Carbonyl Complexes—A New Class of Homogeneous Hydrogenation Catalysts

Y. BLUM, P. CZARKIE, Y. RAHAMIM and Y. SHVO, *Organometallics*, 1985, 4, (8), 1459-1461

$[(\eta^4\text{-Ph}_4\text{C}_5\text{O})(\text{CO})_2\text{Ru}]_2$ and $[(\eta^4\text{-Ph}_2\text{C}_5\text{O})(\text{CO})_2\text{Ru}]_2$ represent a new class of efficient precatalysts for homogeneous hydrogenation of alkenes, alkynes, etc., under moderate conditions.

FUEL CELLS

Application of Carbon Fiber Felts to Air Electrodes for Fuel Cells. II. The Effects of Stacking of Felts, Temperature, and Oxygen Partial Pressure on Discharge Properties

Y. KERA and M. YOKOTA, *Denki Kagaku*, 1985, 53, (8), 601-605

A Zn-air cell was constructed, in which KF-1000 felt with a Pt deposit was applied to the air electrode. Electrode potential was measured under discharge at various constant currents. The drop in terminal voltage was due to the air electrode. The maximum power, evaluated from the p.d. between the two electrodes could be increased up to three-fold by stacking up to 4 felt sheets on top of each other. At 50°C the maximum power increased by 250% over that at 17°C, and replacing air with O₂ gave a further 150% improvement. With 4 sheets of stacked Pt-KF felt in an O₂ stream at 50°C temperature, the maximum power reached 115mW/cm² at $i=170\text{mA}/\text{cm}^2$.

Oxygen-Reducing Electrodes for Acid Fuel Cells

K. V. RAMESH and A. K. SHUKLA, *J. Power Sources*, 1985, 15, (2&3), 201-205

Electrochemical data for O₂ reduction on platinised coconut-shell charcoal electrodes with various Pt loadings in 2.5M H₂SO₄ and 7M H₃PO₄ are reported. The electrodes in both media had good activity and could sustain currents up to 600mA/cm² at a polarisation of ~400mV from their rest potentials.

Electrocatalysis by Ad-Atoms. Part XIII. Preparation of Ad-Electrodes with Tin Ad-Atoms for Methanol, Formaldehyde and Formic Acid Fuel Cells

M. WATANABE, Y. FURUUCHI and S. MOTOO, *J. Electroanal. Chem. Interfacial Electrochem.*, 1985, 191, (2), 367-375

A high specific area Pt electrode with well defined Sn coverage has been developed for use in organic fuel cells. The resulting electrode has enhancement effects in the specific activity over a pure Pt black electrode by a factor of 100 for methanol oxidation, >1000 for formaldehyde oxidation and of 250 for formic acid oxidation. A much higher specific surface area of catalyst is obtained by this simplified preparation.

ELECTRICAL AND ELECTRONIC ENGINEERING

160×244 Element PtSi Schottky-Barrier IR-CCD Image Sensor

W. F. KOSONOCKY, F. V. SHALLCROSS, T. S. VILLANI and J. V. GROPE, *IEEE Trans. Electron Devices*, 1985, **ED-32**, (8), 1564-1573

A 160×244 element i.r. charge coupled device image sensor was developed with 80×40 μm² pixels for operation at 30 frames/s with standard TV face interface. The sensor was developed with PtSi Schottky barrier detectors for 3.0-5.0μm thermal imaging.

Novel Method of Producing Ultrasmall Platinum Silicide Gate Electrodes

P. H. WOERLEE, G. A. M. HURKX, W. J. M. J. JOSQUIN and J. F. C. M. VERHOEVEN, *Appl. Phys. Lett.*, 1985, **47**, (7), 700-702

To produce Pt silicide gate electrodes a novel method using a lateral chemical reaction of Pt with polycrystalline Si at a step edge was developed. The width of the wire is determined by the thickness of a sputtered metal layer. Wires with widths between 35 and 300nm have been produced.

In/Pt Ohmic Contacts to GaAs

D. C. MARVIN, N. A. IVES and M. S. LEUNG, *J. Appl. Phys.*, 1985, **58**, (7), 2659-2661

Graded heterojunction InGaAs ohmic contacts to GaAs with improved electrical and mechanical properties have been produced. The improvements result from the use of a thin Pt layer between the In layer and the 100(GaAs) substrate. This layer moderates the reaction of the In and GaAs producing a uniform contact with lower electrical resistivity.

NEW PATENTS

METALS AND ALLOYS

Creep Resistant Platinum Alloys

OWENS-CORNING FIBERGLAS CORP.

U.S. Patent 4,507,156

The creep resistance of a thermomechanical processed Pt-based alloy, for example yttria dispersion-strengthened Pt, is improved by heating the alloy to at least 2800°F for at least 6 hours.

Resistance Alloy

RESEARCH INSTITUTE OF ELECTRIC & MAGNETIC ALLOYS

U.S. Patent 4,518,439

An electrical resistance alloy having a very low temperature coefficient of resistance over a wide range of temperatures contains 59-88% Pd and 12-41% Fe and is produced by working the material in a specified manner.

TEMPERATURE MEASUREMENT

Properties of Industrial-Grade Platinum-Cobalt Resistance Thermometer between 1 and 27K

H. SAKURAI and L. M. BESLEY, *Rev. Sci. Instrum.*, 1985, **56**, (6), 1232-1235

The stability at 20K of five industrial type Pt-Co resistance thermometers undergoing thermal cycling has been studied, together with their resistance-temperature (R/T) characteristics between 1 and 27K, and their self-heating. The stability at 20K on cycling between room temperature and 20K is ~10mK, and on cycling between 100 and 20K it is a few mK. Differences in the R/T relationship between thermometers were very small, but the self-heating effects are relatively large, particularly at temperatures below 4K.

A Reference Function for Platinum Resistance Thermometer Interpolation between 13.8K and 273.15K

R. C. KEMP, L. M. BESLEY and W. R. G. KEMP, *Metrologia*, 1985, **21**, (3), 139-146

Recent accurate thermodynamic data are combined to provide a basis for a reference function for Pt resistance thermometer interpolation between 13.81K and 273.15K. The values of thermodynamic temperature for defining the fixed points of the IPTS and also for a number of secondary points are more accurately assigned than previously. A temperature scale based on this reference function and these defining fixed points would give thermodynamic temperatures to ±2mK. This system is proposed for use in the revision of the IPTS.

CHEMICAL COMPOUNDS

Tetrarhodium Dodecacarbonyl

DOW CHEMICAL CO.

U.S. Patent 4,514,380

Rh₄(CO)₁₂ is made in less than two hours by reacting RhCl₃ with CO in the presence of activated Cu and a Group IA metal halide and at 25-75°C and a pressure of 3.52-35.2 kg/cm².

ELECTROCHEMISTRY

Electrode Manufacture

PERMELEC ELECTRODE LTD. *British Appl. 2,154,248A*

A liquid composition containing electrode component metal (such as Ru, Pd or Ir) ions and an organic compound capable of forming a complex with the metal ions is thermally decomposed to form an electrode.