

# ABSTRACTS

of current literature on the platinum metals and their alloys

## PROPERTIES

### The Chemistry of Ruthenium, Osmium, Rhodium, Iridium, Palladium and Platinum in the Higher Oxidation States

D. J. GULLIVER and W. LEVASON, *Coord. Chem. Rev.*, 1982, **46**, 1-127

A review is given of papers on the chemistry of platinum group metals in the high oxidation state which is a formal oxidation state of M(IV) or above. The emphasis is placed upon isolated compounds and coverage of solution chemistry is restricted to well-defined species. (1,131 Refs.)

### Hydrogen-Induced Disruption of Oxygen-Doped Platinum Coatings on Glass Microspheres

W. L. PING and S. F. MEYER, *J. Vac. Sci. Technol.*, 1982, **21**, (2), 689-694

Sputter deposited Pt coatings on glass microspheres were severely disrupted after a deuterium-tritium mix was permeated into the hollow spheres at high temperature and pressure. The disruptions were characterised. They suggested that H<sub>2</sub> gas was occluded in the Pt rift structure during the high-pressure filling. Subsequent H<sub>2</sub> pressure release expanded the occluded gas; because diffusion rates were too low to relieve the stress concentrations produced, the Pt coating delaminated along weakly bound interfaces.

### Sound Absorption Properties of Platinum Catalysed Silicone RTV Foam

C. I. LEE and S. SPELLS, *J. Cell. Plast.*, 1982, **18**, (3), 174-177

Pt catalysed silicone RTV foam was examined for its sound absorption properties. It was found to be as good or even better than existing commercial acoustic foams if its density is decreased to 5-6 lb/ft<sup>3</sup>. Incorporating C black into the foam gives an improved sound absorption in a certain frequency range and flame retardancy.

### Reduced Cu-Cr Mixing and Reduced Pt-Cu Interdiffusion by Oxygen in Cu/Cr and Pt/Cu/Cr Thin Films

C.-A. CHANG, *J. Appl. Phys.*, 1982, **53**, (10), 7092-7094

The effects of O<sub>2</sub> on the Pt-Cu and Cu-Cr interdiffusion was studied using Cu/Cr and Pt/Cu/Cr thin film structures. Both processes were reduced by O<sub>2</sub> in agreement with the predicted effects of O<sub>2</sub> by the surface potential model. The Pt-Cu interactions were an example of competing ambient effects dominated by the more electronegative species Pt.

### Detection of Interstitial Hydrogen on Pt/TiO<sub>2</sub> by Means of Conductivity Measurements

H. ZUPEI, C. YIXUAN, L. HUIQING, Y. FENGYUN and W. HONGLI, *J. Catal. (Dalian, China)*, 1982, **2**, (2), 132-135

A large instantaneous change in conductivity of Pt/TiO<sub>2</sub> in H<sub>2</sub> was observed at room temperature. Current carriers for different forms of TiO<sub>2</sub> during thermal treatment in H<sub>2</sub> were produced in different modes. The interaction between H<sub>2</sub> and Pt/TiO<sub>2</sub> is discussed. It is suggested that H<sub>2</sub> is activated and dissociated to H atoms on Pt clusters, it then spills over the TiO<sub>2</sub> as interstitial H which is then ionised and causes the jump in conductivity.

### Effects of Ion-Implantation-Induced Damages and Impurity on Platinum Silicide Formation

Y. MASHIKO, H. KOYAMA, S. KAWAZU and T. KASHIWAKI, *J. Appl. Phys.*, 1982, **53**, (9), 6144-6147

The effects of damages and impurities on the formation of Pt silicide introduced into polycrystalline substrate by ion implantation prior to preparation of metal layer, were studied by spectroscopy. A formation of irregular and nonplanar structure at the Pt silicide/Si interface was observed which was caused by damage.

### Alloying Effects of Palladium. 1966-July, 1982 (Citations from the Metals Abstracts Data Base)

National Technical Information Service, Springfield, VA, PB82-871823, July 1982, pp. 217

A review is given of alloying effects of Pd, and topics include alloying elements, magnetic and physical properties, temperature and pressure effects and corrosion resistance. Mechanical and surface properties, metallic glasses, impurity and composition effects, Curie temperature and superconductivity are included. (283 Refs.)

### Studies of the Structural Diagrams of Cu-Pd-S and Ni-Pd-S

G. N. ZVIADADZE, S. F. GULIANITSKAIA, N. M. PAVLIUCHENKO and N. V. BLAGOVESHCHENSKAIA, *Izv. Akad. Nauk. SSSR, Met.*, 1982, (5), 53-56

Studies were made of the interaction of Pd with Cu sulphides, and partial structural diagrams were constructed for Cu-Pd-S and Ni-Pd-S systems containing ≤ 50 mole% S. In both studied systems, Pd was found in the form of solid solutions with Ni or Cu and also as sulphides PdS and Pd<sub>2</sub>S with dissolved Ni and Cu. Interaction of Pd with Cu sulphides was more active than with Ni sulphides.

## Synthesis and Properties of Phases in $\text{La}_2\text{O}_3\text{-PdO}$

B. G. KAKHAN, V. B. LAZEREV and I. S. SHAPLYGIN, *Zh. Neorg. Khim.*, 1982, **27**, (8), 2090-2093

Studies of oxide phases in the  $\text{La}_2\text{O}_3\text{/PdO}$  system, prepared by heating the  $\text{La}_2\text{O}_3$  and  $\text{Pd}(\text{C}_4\text{N}_2\text{H}_2\text{O}_2)$  oxides in air at 500-810°C, showed the formation of  $\text{La}_2\text{PdO}_4$  and  $\text{La}_2\text{Pd}_2\text{O}_5$ . Crystal structure studies showed that the lattice parameters of  $\text{La}_2\text{PdO}_4$  are  $a = 4.055$  and  $c = 12.62$  Å, and of  $\text{La}_2\text{Pd}_2\text{O}_5$  are  $a = 6.686$  and  $c = 5.616$  Å.

## Bulk Formation of a Metallic Glass: $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$

A. J. DREHMAN, A. C. GREER and D. TURNBULL, *Appl. Phys. Lett.*, 1982, **41**, (8), 716-717

Molten spheroids of  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$  under a vacuum of  $10^{-6}$  torr were slowly cooled at 1.4 K/s on a fused  $\text{SiO}_2$  surface to a form which was glassy except for some superficial crystallinity, of less than 0.5% by volume. Crystallisation was eliminated by surface etching the specimens followed by heating and cooling cycles.

## An X-Ray Study of Domain Structure and Stress in $\text{Pd}_2\text{Si}$ Films at Pd-Si Interfaces

H. CHEN, G. E. WHITE and S. R. STOCK, *Thin Solid Films*, 1982, **93**, (1/2), 161-169

The domain structures of Pd and  $\text{Pd}_2\text{Si}$ , as well as their crystallographic relationship to the Si substrates, were determined on  $\text{Si}(111)$  and  $\text{Si}(100)$  samples by mapping X-ray diffraction pole figures. Elastic and/or plastic deformation in the substrates caused by silicide formation were measured. The stresses in the silicide films were determined from the bending of the Si substrates using X-ray diffraction.

## The Structures and Properties of Some $\text{Rh}_{0.92-x}\text{B}_x\text{Si}_{0.08}$ Metallic Glasses

A. WILLIAMS, M. MEHRA and W. L. JOHNSON, *J. Phys. F*, 1982, **12**, (9), 1861-1868

Rh-based metallic glasses were produced with >40 at.% metalloids (Si and B). X-ray diffraction studies on  $\text{Rh}_{0.92-x}\text{B}_x\text{Si}_{0.08}$  metallic glasses, with  $x = 0.22, 0.27$  and  $0.32$  were performed and mechanical, electrical and thermal analysis data are given. The structural studies showed that this system undergoes great changes at short-range with increasing B concentration.

## Thermal Stability of Iridium Chlorides

I. M. SINITSIN, V. V. BORISOV and A. S. KOZLOV, *Zh. Neorg. Khim.*, 1982, **27**, (9), 2322-2328

The thermal stability of  $\text{IrCl}_3$ ,  $\text{K}_3[\text{IrCl}_6]$ ,  $\text{K}_2[\text{IrCl}_6]\cdot\text{H}_2\text{O}$ ,  $\text{K}_3[\text{Ir}(\text{H}_2\text{O})\text{Cl}_4]$  and  $\text{K}_4[\text{Ir}_2\text{Cl}_{10}]$  was studied in air, Ar and  $\text{Cl}_2$ . Chemical and phase conversions occurring during chlorination of Ir in the presence of KCl were also investigated. High-temperature X-ray phase analysis of basic intermediate products of thermal dissociation of  $\text{K}_3[\text{IrCl}_6]$  showed the existence of high temperature modification with reverse polymorphic transfer at 485°C.

## Chemical Vapour Transport of Transition-Metal Oxides. II. Epitaxial Growth of $\text{RuO}_2$ , $\text{IrO}_2$ and $(\text{Ru}_{1-x}\text{Ir}_x)\text{O}_2$ on $\text{TiO}_2$

P. TRIGGS, C. A. GEORG and F. LÉVY, *Mater. Res. Bull.*, 1982, **17**, (5), 671-679

Epitaxial growth of  $\text{RuO}_2$  and  $\text{IrO}_2$  has been performed by chemical vapour transport on  $\text{TiO}_2$  substrates. Two types of samples were found. The first showed epitaxial layers of the Ru and Ir oxides with orientations close to that of the substrate, and with low level interdiffusion of the components. The second shows no epitaxial growth but the incorporation of Ru and Ir into the substrate surface giving a brown colouration.

## CHEMICAL COMPOUNDS

### Synthesis and Properties of Platinum Metal Oxides of the Type $\text{M}_x\text{Pt}_3\text{O}_4$

R. D. SHANNON, T. E. GIER, P. F. CARCIA, P. E. BIERSTEDT, R. B. FLIPPEN and A. J. VEGA, *Inorg. Chem.*, 1981, **21**, (9), 3372-3382

Methods were developed for high yield syntheses of  $\text{M}_x\text{Pt}_3\text{O}_4$  where  $\text{M} = \text{Li}, \text{Na}, \text{Mg}, \text{Ca}, \text{Zn}, \text{Cd}, \text{Co}$  and  $\text{Ni}$ . Vapour phase hydrolysis of chloride mixtures produces samples with surface areas of 10-40  $\text{m}^2/\text{g}$  and has yielded compositions  $\text{H}_x\text{Pt}_3\text{O}_{4-y}\text{Cl}_y$  and  $\text{Ni}_x\text{Pt}_3\text{O}_{4-y}\text{Cl}_y$ , probably the first example of insertion of H and Cl into the  $\text{M}_x\text{Pt}_3\text{O}_4$  lattice. Plots of cell dimensions,  $a$  vs.  $x$  for  $\text{Na}_x\text{Pt}_3\text{O}_4$ ,  $\text{Cd}_3\text{Pt}_3\text{O}_4$ ,  $\text{Mg}_x\text{Na}_y\text{Pt}_3\text{O}_4$ ,  $\text{Co}_x\text{Na}_y\text{Pt}_3\text{O}_4$  and  $\text{Ni}_x\text{Na}_y\text{Pt}_3\text{O}_4$  are given. Magnetic susceptibility and XPS data are given. Metallic conductivity in  $\text{NaPt}_3\text{O}_4$ ,  $\text{Ni}_{0.2}\text{Pt}_3\text{O}_4$  and  $\text{Li}_{0.8}\text{Pt}_3\text{O}_4$  is consistent with short Pt-Pt bonds and conflicts with recent claims of semiconducting behaviour.

### Disulfur and Diselenium Complexes of Rhodium and Iridium

A. P. GINSBERG, W. E. LINDSELL, C. R. SPRINKLE, K. W. WEST and R. I. COHEN, *Inorg. Chem.*, 1982, **21**, (10), 3666-3681

A review of Rh and Ir complexes which cleave  $\text{S}_8$  and  $\text{Se}_8$  rings to form complexes with the fragments is given. The syntheses are stated and the complexes formed are characterised. (79 Refs.)

## ELECTROCHEMISTRY

### Investigation on the Electrocatalytic Dehydrogenation of CHO-Compounds in Acidic Media via a Palladium Membrane

W. GÜTHER and W. WIELSTICH, *Electrochim. Acta*, 1982, **27**, (7), 811-816

The dehydrogenation of formic acid, formaldehyde and methanol was studied using a  $\text{H}_2$  diffusion membrane. The catalytic effect of Pt was followed via the electrodeposition of this electrocatalyst on one side of the Pd membrane.

### Corrosion of Platinum Catalyst in Alkaline Solutions

V. S. BAGOTZKY, E. I. KHRUSHCHEVA, M. R. TARASEVICH and N. A. SHUMILOVA, *J. Power Sources*, 1982, **8**, (243), 301-309

The corrosion behaviour, as affected by time and potential of Pt black in alkaline solution at 20 and 70°C has been studied. Over the range 0.85-1.37V Pt undergoes dissolution, the maximum corrosion rate being at 0.93-0.95V. With time the corrosion current decreases to  $10^{-6}$ - $10^{-7}$  A/m<sup>2</sup>. When Pt passes into solution the complex ion  $[\text{Pt}(\text{OH})_2]^{2-}$  is formed. The influence of Pt pretreatment on the corrosion rate was investigated, and  $\text{Ba}^{2+}$  ions were found to slow down the dissolution process, while  $\text{Cl}^-$  ions increased its rate.

### Preparation and Characterisation of a New Electrode of the Type $\text{Ti}/\text{PtO}_x/\text{TiO}_2$

CH. COMINELLIS and E. PLATTNER, *Oberflaeche-Surf.*, 1982, **23**, (9), 315-318

The electrode  $\text{Ti}/\text{PtO}_x/\text{TiO}_2$  in dilute HCl has been studied as a function of the relative composition of the two oxides thermally deposited at different temperatures. It has been found that the maximum for catalytic activity of the electrode for discharge of chlorine is at a ratio  $\text{PtO}_x:\text{TiO}_2$  of 10:1.

### An Investigation of the Hydrogen Permeation through the $\alpha/\beta$ Phase Palladium by the Electrochemical Method

Y. SAKAMOTO, M. KAWACHI and S. HIRATA, *J. Jpn. Inst. Met.*, 1982, **46**, (5), 530-537

The  $\text{H}_2$  permeation rate through annealed and cold rolled Pd foil under various current densities to form a region of co-existence of  $\alpha$ -Pd and  $\beta$ -Pd phase hydride was measured at  $299 \pm 1$  K by the electrochemical permeation method. The rate determining step for the permeation was examined as a  $\text{H}_2$ -diffusion process in the remaining  $\alpha$ -phase Pd of the matrix accompanying the  $\alpha/\beta$ -Pd phase transformation. Adding  $\text{H}_2\text{SeO}_3$  to the electrolyte for cathodic polarisation strongly inhibited the discharge step of H ions for both Pd specimens, but scarcely influenced the H permeation behaviour.

### Cathodic $\text{H}_2$ Gas Production through Pd Alloy Membrane Electrodes

T. SHIROGAMI and K. MURATA, *Int. J. Hydrogen Energy*, 1982, **7**, (11), 877-882

A  $\text{H}_2$  permeable membrane electrode (HPME)- $\text{H}_2$ -NiOOH rechargeable cell was tested to aid development of a high performance  $\text{H}_2$ -metal oxide cell. A 66.6wt.%Pd-13.4wt.%Ag-20wt.%Au alloy membrane with one surface covered with Pd-Pt black catalyst and the other with Pd black was used as one of the walls of the vessel. When the Pd-Pt catalysed electrolyte-facing surface is cathodically polarised in concentrated KOH solution, H atoms dissolve in the membrane by penetrating it and leave the other (palladised) surface as free  $\text{H}_2$ .

### Electrochemical Activity of Dispersed Palladium-Silver Alloys during Production and Ionisation of Hydrogen

ZH. L. VERT, V. F. PAVLOVA and I. P. TVERDOVSKII, *Electrokhimiya*, 1982, **18**, (8), 1055-1058

Electrochemical activity of Pd-Ag alloys was studied during ionisation and production of  $\text{H}_2$  from acidic and alkaline solutions by a polarisation method. Comparison was made of calculated current exchanges with constant values of the rate of hydrogenation of maleic acid on Pd-Ag alloys, and with electrochemical properties of solid Pd-Cu and Pd-Pt solutions.

### Metal Oxide Anodes for Oxygen Evolution

H. TAMURA and C. IWAKURA, *Int. J. Hydrogen Energy*, 1982, **7**, (11), 857-865

The kinetics of anodic dissolution and  $\text{O}_2$  evolution at a Ru electrode in acidic solution were studied. Hydrous and anhydrous  $\text{RuO}_2$  electrodes were prepared by heating hydrous  $\text{RuO}_2$  samples at 90-1000°C, and their anodic characteristics were studied in connection with their physical properties. The anodic characteristics of the  $\text{Ti}/\text{RuO}_2$  electrode, especially the cause of its activity loss during  $\text{O}_2$  evolution were studied.

### Metallic Clusters in Solid Solutions of $\text{Ti}_{1-x}\text{Ru}_x\text{O}_2$ and Electrochemical Properties of Oxidised Ruthenium-Titanium Anodes

IU. E. ROGINSKAIA, B. SH. GALIAMOV, I. D. BELOVA, R. R. SHIFRINA, V. B. KOZHEVNIKOV and V. I. BYSTROV, *Electrokhimiya*, 1982, **18**, (10), 1327-1334

Spectroscopic and electrophysical studies of the structure of the active layer of oxidised Ru-Ti anodes and of  $\text{Ru}_x\text{Ti}_{1-x}\text{O}_2$  solid solutions showed the formation of elongated clusters with metallic properties at  $x < 0.25$  while at  $x > 0.25$  these agglomerate into infinite clusters. A strong interaction observed between the metallic components and  $\text{TiO}_2$  resulted in the occurrence of electronic density 3d-state in  $\text{TiO}_2$ .

## PHOTOCONVERSION

### Photoelectrochemical Behavior of n-Si Electrodes Protected with Pt-Polypyrrole

T. SKOTHEIM, I.-G. PETERSSON, O. INGANAS and I. LUNDSTRÖM, *J. Electrochem. Soc.*, 1982, **129**, (8), 1737-1741

Highly stable photoanodes based on single crystal n-Si protected with a thin coating of Pt and electrochemically grown polypyrrole films have been studied. A power conversion efficiency of 5.5% under illumination by a W halogen light occurred with an iodide/triiodide electrolyte. The cells are stable for several weeks. The junctions show almost ideal Schottky junction behaviour. (41 Refs.)

### Photoassisted Water-Gas Shift Reaction on Platinized Titania. The Influence of Preparation Parameters

S.-M. FANG, B.-H. CHEN and J. M. WHITE, *J. Phys. Chem.*, 1982, **86**, (16), 3126-3130

The variation in the rate of the photoassisted water-gas shift reaction over Pt/TiO<sub>2</sub> with changes in catalyst preparation were studied. The reaction rate: is independent of the Pt deposition method, is first order in light intensity, is independent of the chemical state or the Pt loading above 2wt.%, depends on reduction of the TiO<sub>2</sub> and is strongly dependent on surface concentration of NaOH. It is concluded that with NaOH present, the rate limiting step is the reaction of photoproduced holes with surface OH<sup>-</sup> ions.

### Photopotential Behaviour of Platinized TiO<sub>2</sub> Particles

K. UOSAKI and H. KITTA, *J. Electrochem. Soc.*, 1982, **129**, (8), 1752-1753

The photoeffect of a Xe lamp on the potential of platinised TiO<sub>2</sub> particle catalysts suspended in NaOH solution is reported. The potential does not exceed some steady value at which the rate of electron excitation equals that of electron consumption by the reaction with H<sub>2</sub>O plus the recombination. The steady potential is positive compared with the reversible H electrode potential, suggesting no H evolution at atmospheric pressure.

### Excited-State Photoelectrochemical Cells for the Generation of H<sub>2</sub> and O<sub>2</sub> Based on Ru(bpy)<sub>3</sub><sup>2+</sup>\*

W. J. DRESSICK, T. J. MEYER, B. DURHAM and D. P. RILLEMA, *Inorg. Chem.*, 1982, **21**, (9), 3451-3458

Excited-state photoelectrochemical cells are described for the production of H<sub>2</sub> or O<sub>2</sub> (or I<sub>2</sub>) in aqueous solution. The cells are based on visible excitation of Ru(bpy)<sub>3</sub><sup>2+</sup> followed by oxidative quenching of the resultant charge-transfer excited state(s). In the H<sub>2</sub> cell the quencher is paraquat. In the O<sub>2</sub>(or I<sub>2</sub>) cell, Co<sup>III</sup>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub><sup>3-</sup> acts as a quencher. Descriptions of the functions of the quenchers, variation in photocurrents in the cells as functions of pH, quencher and scavenger concentration are given.

### Photoelectrochemistry of Ru(bpy)<sub>3</sub><sup>2+</sup> in Basic Medium at SnO<sub>2</sub> and Metal Electrodes

A. KIRSCH-DE MESMAEKER, J. NASIELSKI and R. WILLEM, *Bull. Soc. Chim. Belg.*, 1982, **91**, (9), 731-742

The effect of the pH on the photoelectrochemical behaviour of Ru(bpy)<sub>3</sub><sup>2+</sup> is examined at a highly doped SnO<sub>2</sub> electrode. An important photocurrent increase from pH 11 to 13 is explained by the photochemical production of a long-lived reductant generated from Ru(bpy)<sub>3</sub><sup>2+</sup>. Photocurrent observations at metallic electrodes and the photogalvanic cell behaviour confirm this interpretation.

### Photo-Induced Hydroxide Addition to Nitrosyl Group of Bis (2,2'-Bipyridine)-Chloronitrosylruthenium(2+) in Aqueous Solution

A. SUGIMORI, H. UCHIDA, T. AKIYAMA, M. MUKAIDA and K. SHIMIZU, *Chem. Lett.*, 1982, (8), 1135-1138

A novel photoreactivity of [RuCl(bpy)<sub>2</sub>NO]<sup>2+</sup> in aqueous solution at pH ≈ 5 by u.v. or solar light is reported. Hydroxide is added to a co-ordinating NO to give metastable [RuCl(bpy)<sub>2</sub>NO<sub>2</sub>H]<sup>+</sup> which returns to [RuCl(bpy)<sub>2</sub>NO]<sup>2+</sup> in the dark. The reaction gives a reversible change of H<sup>+</sup> concentration. Quantum yields at various irradiation wavelengths are given.

### ELECTRODEPOSITION AND SURFACE COATINGS

#### Deposition of Palladium from an Acid Electrolyte

F. SIMON and W. ZILSKE, *Galvanotechnik*, 1982, **73**, (9), 981-982

A new Pd bath is described from which coatings with low H content and low internal stresses can be deposited. The coatings have high corrosion resistance and wear resistance and can, in many cases, replace hard gold. A typical example of this is in the field of plug connections for low current technology. The Pd electrolyte contains 2-15 g/l Pd, 0.5-2 g/l Pd as a sulphite complex and 100 g/l acid concentration. The properties of the deposition and of the H content are discussed. A H:Pd ratio of 0.0004 : 1 can be achieved.

### LABORATORY APPARATUS AND TECHNIQUE

#### On the Theory and Use of a New Fast-Response Dissolved Hydrogen Probe for Hydrogen Transfer Studies

B. ANDERSSON and T. BERGLIN, *Chem. Eng. J.*, 1982, **24**, (2), 201-212

A fast response H<sub>2</sub> analogue to the well-known membrane-covered O<sub>2</sub> electrode was constructed, based upon anodic oxidation of H<sub>2</sub> on Pt in concentrated H<sub>2</sub>SO<sub>4</sub>. The hydrogen probe was also found to serve as an excellent chromatograph H<sub>2</sub> flow-cell detector.

#### A Novel Hydrogen Gas Sensor Based on Hydrogen Uranyl Phosphate

J. S. LUNDGAARD, J. MALLING and M. L. S. BIRCHALL, *Solid State Ionics*, 1982, **7**, (1), 53-56

Porous composite electrodes of Pt and Pd are used in a novel H<sub>2</sub> gas sensor with layered hydrate H<sub>2</sub>UO<sub>2</sub>PO<sub>4</sub>·4H<sub>2</sub>O. The conductivity is dependent on the pressure of water vapour, and long term stability is obtained even at current densities as high as 5 mA/cm<sup>2</sup>. The Pt and Pd electrodes in the cells gave correct voltages according to Nernst's law.

## Pd-InP Schottky Diode Hydrogen Sensors

M. YOUSUF, B. KULIYEV, B. LALEVIC and T. L. POTEAT, *Solid-State Electron.*, 1982, **25**, (8), 753-758

Pd-InP Schottky diodes are very sensitive and reproducible detectors of H<sub>2</sub>. Absorption or desorption of H<sub>2</sub> by Pd causes large changes in the diode C-V or I-V characteristics.

## Conducting MIS Diode Gas Detectors: The Pd/SiO<sub>2</sub>/Si Hydrogen Sensor

S. J. FONASH, H. HUSTON and S. ASHOK, *Sens. Actuators*, 1982, **2**, (4), 363-369

A survey of barrier formation and transport in MS and conducting MIS structures is presented and used to describe the H<sub>2</sub> sensitivity of Pd/SiO<sub>2</sub>/Si structures. The presence of the interfacial oxide is necessary for the Pd diode to be sensitive to H<sub>2</sub>. The sensitivity of highly responsive devices is due to Schottky barrier modification in the presence of H<sub>2</sub> and not to an additional channel of transport caused by an increased interface state density in H<sub>2</sub>.

## HETEROGENEOUS CATALYSIS

### Catalytic Combustion of Hydrogen. IV. Fabrication of Prototype Catalytic Heaters and Their Operating Properties

M. HARUTA and H. OSANO, *Int. J. Hydrogen Energy*, 1982, **7**, (10), 801-807

Two prototypes of catalytic heaters operating on H<sub>2</sub> were constructed. The H<sub>2</sub> fuelled catalytic heater offers an adjustable heat output of 0-1.5 kcal/cm<sup>2</sup>h with Pt impregnated Ni foam as a catalyst. Studies of local combustion efficiency and local amounts of air entrained from the ambience were made.

### Bimetallic Catalysts; Application in Catalytic Reforming

J. L. CARTER, G. B. McVICKER, W. WEISSMAN, W. S. KMAK and J. H. SINFELT, *Appl. Catal.*, 1982, **3**, (4), 327-346

The results of various studies on Pt-Ir and Pt-Re reforming catalysts are reported. The studies include catalyst characterisation by H<sub>2</sub> and CO chemisorption, catalyst comparisons for conversion of selected hydrocarbons and extended runs on the reforming of petroleum naphtha fractions.

### Catalytic Performance of Egg White Type Pt/Al<sub>2</sub>O<sub>3</sub> Catalyst in the Oxidation of C<sub>3</sub>H<sub>8</sub> and CO

K. KUNIMORI, I. NAKAJIMA and T. UCHIJIMA, *Chem. Lett.*, 1982, (8), 1165-1168

An egg white type Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, without any Pt on the exterior surface, was prepared and the catalytic activities for C<sub>3</sub>H<sub>8</sub> and CO oxidation were compared with conventional egg shell and uniform type catalysts. For the CO oxidation, it was confirmed that the egg white type catalyst was more active than the egg shell type.

## Metal Surface Areas of Platinum-Rhenium Catalysts

V. ESKINAZI, *Appl. Catal.*, 1982, **4**, (1), 37-40

H<sub>2</sub> and O<sub>2</sub> chemisorption and H<sub>2</sub> titration measurements were used to characterise the surface structure and find the degree of interaction between Pt and Re on Pt-Re/Al<sub>2</sub>O<sub>3</sub> catalysts. The effects of surface support area and calcination conditions on metal dispersion were also investigated. Maximum metal surface areas were obtained with 55 mole% Re/Al<sub>2</sub>O<sub>3</sub> supports with surface areas greater than 150 m<sup>2</sup>/g and with catalyst pretreatment involving a 500°C air calcination before reduction.

## Selective Reduction of Nitrogen Monoxide with Hydrogen on Pt/Al<sub>2</sub>O<sub>3</sub> Containing a Metal Oxide

Y. KOSAKI, A. MIYAMOTO and Y. MURAKAMI, *Bull. Chem. Soc. Jpn.*, 1982, **55**, (6), 1719-1726

The NO-H<sub>2</sub> reaction on a Pt-V<sub>2</sub>O<sub>5</sub>/Al<sub>2</sub>O<sub>3</sub> three-way catalyst was composed of three main steps. Step I, the formation of NH<sub>3</sub> by the reduction of NO with H<sub>2</sub> on Pt; Step II, the NO-NH<sub>3</sub> reaction on Pt to form N<sub>2</sub> or N<sub>2</sub>O; and Step III, the reduction of V<sub>2</sub>O<sub>5</sub> in the catalyst by H<sub>2</sub> which is accelerated by "H<sub>2</sub> spillover". In the NO-H<sub>2</sub> reaction on the Pt-V<sub>2</sub>O<sub>5</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst, the formation of excess NH<sub>3</sub> is suppressed by the removal of H<sub>2</sub> from Pt in Step III, and the NH<sub>3</sub> thus produced reacts with NO to form N<sub>2</sub> or N<sub>2</sub>O selectively in Step II.

## Properties of Platinum Supported on Oxides of Titanium

B.-H. CHEN and J. M. WHITE, *J. Phys. Chem.*, 1982, **86**, (18), 3534-3541

Pt supported on TiO<sub>2</sub>, TiO and Ti<sub>2</sub>O<sub>3</sub> in various forms has been investigated by several techniques. On H<sub>2</sub>-pretreated TiO<sub>2</sub>, on TiO and on Ti<sub>2</sub>O<sub>3</sub> platinised samples, strong metal-support interactions (SMSI) with limited H<sub>2</sub> uptake was noted. Very fast H-for-D exchange was observed on all materials, showing that dissociative adsorption still occurs. It was concluded that surface contamination, Pt diffusion into the bulk oxide, formation of surface mixed metal oxides and metal agglomeration do not significantly contribute to loss of H<sub>2</sub> uptake capacity. The SMSI effect may be best understood in terms of a bulk oxide reduction.

## Acidity and Catalytic Activity of RECaY Zeolites for Toluene Disproportionation

R. P. DIMITROVA, C. DIMITROV, Z. POPOVA and K. H. STEINBURG, *Appl. Catal.*, 1982, **3**, (4), 377-380

The conversion of toluene was studied on three series of zeolite catalysts based on CaY, RECaY and Pt/RECaY. A relationship was observed between demethylation and disproportionation, and the concentrations of the active sites with acidity  $-8.2 \leq \text{p}K_a \leq -5.6$ , and  $-5.6 \leq \text{p}K_a \leq -3.0$ , respectively, for the CaY and RECaY series. Pt supported catalysts when tested under identical conditions show higher activity and selectivity.

## Adsorption of Benzene during Benzene Hydrogenation over Palladium/Alumina Catalyst

K. NAKANO and K. KUSUNOKI, *Kagaku Kagaku Ronbunshu*, 1982, **8**, (2), 162-167

To clarify the adsorption amounts and adsorption sites of organic species during  $C_6H_6$  hydrogenation, adsorption measurements of  $C_6H_6$  and cyclohexane on Pd/Al<sub>2</sub>O<sub>3</sub> catalysts were made at 108-175°C using an electrobalance. Reversible adsorption on the Al<sub>2</sub>O<sub>3</sub> support was predominant and the amount adsorbed on Pd was negligibly small under a H<sub>2</sub> atmosphere during  $C_6H_6$  hydrogenation. A reversible adsorption on Pd atoms and irreversible adsorption exist as well as the reversible adsorption on the support under H<sub>2</sub>-free conditions. Thus  $C_6H_6$  hydrogenation appears to occur between H<sub>2</sub> adsorbed on metal atoms and  $C_6H_6$  adsorbed reversibly on the Al<sub>2</sub>O<sub>3</sub> support situated near the metal-support boundary.

## Effect of Particle Size on the Activity of Supported Palladium Catalysts

Y. TAKASU, T. AKIMARU, K. KASAHARA and Y. MATSUDA, *J. Am. Chem. Soc.*, 1982, **104**, (19), 5249-5250

The effect of particle size in a Pd/C catalyst on the kinetics of the H<sub>2</sub>-D<sub>2</sub> exchange reaction at up to 30°C and at  $2.8 \times 10^{-2}$  torr pressure was studied. The catalyst was the first to be prepared in situ in an UHV system and to have electronic energy levels characterised by XPS. As average particle diameter,  $\bar{d}$ , increases the activation energy for the exchange reaction declines from 50 kJ/mol at  $\bar{d} = 1.1$  nm to 20 kJ/mol at 1.8 nm. It is postulated that as particle size increases and the binding energy of the core and valence electrons within the Pd particles increases, adsorption energy of H<sub>2</sub> on the Pd decreases.

## A Silica-Supported Inorganic Photosensitizer

P. A. GRUTSCH and C. KUTAL, *J. Chem. Soc., Chem. Commun.*, 1982, (16), 893-894

Adsorbing [Ir(bipy)<sub>3</sub>OH]<sup>2+</sup> (bipy = 2,2'-bipyridine) onto the surface of silica gel gives a highly efficient heterogeneous photosensitizer for the valence isomerisation of norbornadiene to quadricyclene.

## Catalytic Hydrogenation of Ethylene with (H)Os<sub>3</sub>(CO)<sub>10</sub>OSi≡. Spectroscopic Evidence for a Cluster Catalysed Reaction

A. BESSON, A. CHOPLIN, L. D'ORNELAS and J. M. BASSET, *J. Chem. Soc., Chem. Commun.*, 1982, (15), 843-845

(H)Os<sub>3</sub>(CO)<sub>10</sub>(OSi≡) is a catalyst for C<sub>2</sub>H<sub>4</sub> hydrogenation at 353K. Evidence is presented for the reversibility of C<sub>2</sub>H<sub>4</sub> co-ordination with the cluster and for the complete catalytic cycle of C<sub>2</sub>H<sub>4</sub> hydrogenation. This is the first case of catalysis by a molecular cluster grafted onto unmodified SiO<sub>2</sub>. The absence of catalyst ageing may be due to the grafting, which may stabilise co-ordinate unsaturation and avoid secondary reactions.

## Natural Gas from Carbon Dioxide

*New Sci.*, 1982, **95**, (1324), 831

A new Ru carbonyl metal cluster catalyst makes natural-quantity gas from gasified coal. It not only hydrogenates CO but also hydrogenates a waste product of the process, CO<sub>2</sub>. With a 4:1 mix of H<sub>2</sub>:CO<sub>2</sub> at 1 atm and 275°C, CH<sub>4</sub> yields are 60-70% on one pass of gas mixture. Higher yields may be possible at higher pressures.

## Carbon Dioxide and Carbon Monoxide Methanation by Supported Ruthenium Catalysts

H. E. FERKUL, D. J. STANTON, J. D. McCOWAN and M. C. BAIRD, *J. Chem. Soc., Chem. Commun.*, 1982, (16), 955-956

Ru carbonyl clusters adsorbed on oxide supports and thermally decomposed under H<sub>2</sub>, are very active catalysts for the methanation of both CO and CO<sub>2</sub>.

## HOMOGENEOUS CATALYSIS

### Transition Metals in Organic Synthesis; Annual Survey Covering the Year 1980

L. S. HEGEDUS, *J. Organomet. Chem.*, 1982, **237**, (1), 231-451

A review is given of the C-C bond forming reactions, including alkylations of organic halides, acid halides, olefins, alkynes, alcohols and acetates, carbonyl compounds, epoxides, dienyl complexes, coupling and cycloaddition reactions, all using various platinum group metals catalysts. Conjugate addition, carbonylation, oligomerisations, rearrangements, oxidations, reductions and functional group preparations are also surveyed. (1,045 Refs.)

### Catalytic Oxidative Chlorination of n-Pentane by Platinum Complexes

W. YUBIN and D. FUGUAN, *J. Catal. (Dalian, China)*, 1982, **3**, (2), 144-146

Catalytic oxidative chlorination of n-pentane by Pt(II) complexes, [PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], [PtHCl(PPh<sub>3</sub>)<sub>2</sub>], [PtHBr(PPh<sub>3</sub>)<sub>2</sub>], [PtHI(PPh<sub>3</sub>)<sub>2</sub>], [PtCOCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] and K<sub>2</sub>PtCl<sub>4</sub> under mild conditions was studied using H<sub>2</sub>PtCl<sub>6</sub> and K<sub>2</sub>PtCl<sub>6</sub> as oxidants. The Pt(II)(catalyst)-Pt(IV)(oxidant) system is not only effective for catalysing the title reaction, but is also more active in the impregnated form on a carrier.

### Transition-Metal-Catalysed Oxidation of Carbon Monoxide by Dichlorine to Produce Phosgene

F. CALDERAZZO and D. BELLI DELL'AMICO, *Inorg. Chem.*, 1982, **21**, (10), 3639-3642

Halometal carbonyls of Pt, Pd and Au catalysed the formation of COCl<sub>2</sub> from CO and Cl<sub>2</sub> at atmospheric pressure and room temperature under exclusion of light. Attack at the carbonyl C of soluble halo-carbonyl complexes by co-ordinated chloride or Cl<sub>2</sub> to give M-C(O)-Cl groupings is thought to be the process involved.

### General Synthetic Route for SO<sub>2</sub> Cluster Compounds of Platinum and the Structural Characterisation of Pt<sub>5</sub>(μ-CO)<sub>2</sub>(μ-SO<sub>2</sub>)<sub>3</sub>(CO)(PPh<sub>3</sub>)<sub>4</sub>

C. E. BRIANI, D. G. EVANS and D. M. P. MINGOS, *J. Chem. Soc., Chem. Commun.*, 1982, (2), 1144-1146

The reaction of 1 atm of SO<sub>2</sub> at 60°C with toluene solutions of Pt carbonyl cluster compounds provides a general synthetic route for Pt SO<sub>2</sub> cluster compounds.

### A Rh Cluster which Selectively Reduces Aldehyde Functions Using CO and H<sub>2</sub>O as the Hydrogen Source

K. KANEDA, M. YASUMURA, T. IMANAKA and S. TERANISHI, *J. Chem. Soc., Chem. Commun.*, 1982, (16), 935-936

The Rh<sub>6</sub>(CO)<sub>16</sub>-N,N,N',N'-tetramethyl-1,3,3-propanediamine catalyst system has high activity for the reduction of aldehydes using CO and H<sub>2</sub>O as the H<sub>2</sub> source; unsaturated aldehydes give the corresponding unsaturated alcohols in high yields.

### Reactivity and Selectivity in Catalysis by Rhodium Complexes

J. M. BROWN, *Chem. Ind.*, 1982, (19), 737-741

Homogeneous and asymmetric homogeneous reactions, olefin isomerisation, internal asymmetric induction hydroformylation and decarbonylation by organorhodium complex catalysts are discussed. The reactions involve a series of linked intermediates where H<sub>2</sub>, an olefin and possibly CO are simultaneously co-ordinated and undergo rearrangement.

### Activating Hydrogen with Iridium Compounds

R. H. CRABTREE, *Chemtech*, 1982, 12, (8), 506-512

A review of Ir homogeneous catalysts is presented. The use of the catalysts in hydrogenation and dehydrogenation reactions, reaction conditions and mechanisms, ligands tested and product yields are discussed. H-bridged cluster compounds and alkane activation systems were examined and *t*-butyl ethylene was found to weakly bind the metal but also to be very reactive, stripping H from organometals. (34 Refs.)

### Ruthenium-Catalysed Reduction of Carbonyl Compounds Using Formic Acid

Y. WATANABE, T. OHTA and Y. TSUJI, *Bull. Chem. Soc. Jpn.*, 1982, 55, (8), 2441-2444

Carbonyl compounds were hydrogenated to the corresponding alcohols in excellent yields using formic acid with a Ru complex at 125°C for 3 h. 2-Propanone was reduced to 2-propanol by the RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>-HCOOH system in 94% yield with 98% selectivity. The catalytic activity was found to decrease in the order RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>, RuHCl(PPh<sub>3</sub>)<sub>3</sub>, RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> and RuH<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>.

### Effect of Added Ru<sub>3</sub>(CO)<sub>12</sub> on the Indirect Hydrogenation of Cellulose

J. D. COTTON, J. C. PENROSE and P. R. WELLS, *Fuel*, 1982, 61, (9), 873-874

The addition of small amounts of Ru<sub>3</sub>(CO)<sub>12</sub> to a mixture of a cellulose substrate, Na<sub>2</sub>CO<sub>3</sub>, CO and H<sub>2</sub>O significantly enhances the extent of the conversion and the H:C ratio in the oil produced in its indirect hydrogenation at 250-350°C. However, the O<sub>2</sub> content of the oil is slightly higher.

### Catalytic Oxidation of Water by an Oxo-Bridged Ruthenium Dimer

S. W. GERSTEN, G. T. SAMUELS and T. J. MEYER, *J. Am. Chem. Soc.*, 1982, 104, (14), 4029-4030

An oxo-bridged dimeric system of Ru(III), [(bpy)<sub>2</sub>(H<sub>2</sub>O)RuORu(H<sub>2</sub>O)(bpy)<sub>2</sub>]<sup>4+</sup>, on oxidation by 4 equivalents, (electrochemically or via Ce(IV)) leads to the rapid oxidation of H<sub>2</sub>O. After catalysis the dimer was present in its Ru(III), Ru(IV) form. 50-fold and 100-fold excesses of Ce(IV) were used.

## FUEL CELLS

### Engineering Analysis of an NH<sub>3</sub>-Air Fuel Cell System for Vehicles

P. N. ROSS, *Electrochem. Soc. Symp.*, Detroit, Oct. 1982, Extended Abstract No. 288, p. 467

An alkaline fuel cell for vehicles using anhydrous liquid NH<sub>3</sub> as the H<sub>2</sub> storage medium and cracked NH<sub>3</sub> as the anode feed, with supported Pt PAFC-type electrodes containing 0.15 mg Pt/cm<sup>2</sup> on the anode and 0.35 mg Pt/cm<sup>2</sup> on the cathode is described. Power consumption, mass and energy balances for the system are described. NH<sub>3</sub> is stored as saturated liquid, is vapourised, superheated and fed to the reactor for H<sub>2</sub> generation.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Effects of Interface Structure on Electrical Characteristics of PtSi-Si Schottky Barrier Contacts

S.-Y. TSAUR, D. J. SILVERSMITH, R. W. MOUNTAIN and C. H. ANDERSON, *Thin Solid Films*, 1982, 93, (3/4), 331-340

The properties of PtSi-Si Schottky barrier contacts formed by a new technique employing multilayer metallisation are studied. The multilayer technique permits the formation of very shallow contacts without any limitation in the thickness of the PtSi layer. The interfacial uniformity is independent of PtSi thickness for shallow PtSi-Si contacts produced by this technique. Larger area (9.4 × 10<sup>-3</sup> cm<sup>2</sup>) diodes utilising shallow PtSi-Si contacts about 200 Å deep were fabricated without guard rings. These diodes exhibit near-ideal forward current-voltage characteristics, low reverse leakage currents and high breakdown voltages.

## Reduction in the Effective Barrier Height in PtSi-p-Si Schottky Diodes by Using Low Energy Ion Implantation

C.-Y. WEI, W. TANTRAPORN, W. KATZ and G. SMITH, *Thin Solid Films*, 1982, **93**, (3/4), 407-412

A reduction in the effective barrier height in a PtSi-p-Si Schottky diode was achieved by low energy implantation, to introduce a shallow Pt layer on a p-Si substrate. After the Schottky diode was implanted with  $3 \text{ keV}^{11}\text{B}^+$  ions to a dose of  $4 \times 10^{12}$  ions/cm<sup>2</sup>, the barrier height was observed to decrease from 0.26 to 0.16 eV.

## Preparation of a RuO<sub>2</sub>-Modified Semiconductor Oxide Surface. An Optimization Procedure of Interest in Energy Conversion Systems

I. D. BURKE, J. F. HEALY and O. NI DHUBHGHAILL, *Surf. Technol.*, 1982, **16**, (4), 341-347

A simple procedure is described for modifying the surface of a semiconducting or insulating oxide powder (such as TiO<sub>2</sub>) by the adsorption of RuCl<sub>3</sub> from isopropanol solution. Adsorption at monolayer and submonolayer level was readily achieved, 1 g of Ru being uniformly dispersed as RuCl<sub>3</sub> or RuO<sub>2</sub> over 9000 m<sup>2</sup> of the surface of a TiO<sub>2</sub> support. Heating the powder in air at 425°C resulted in the formation of a RuO<sub>2</sub>-modified surface. The surface-bonded RuO<sub>2</sub> groups were shown to be active with respect to catalytic oxidation reactions, and repeated runs with the same catalyst confirmed the stability of the RuO<sub>2</sub> linkage to the oxide support.

## Strange Temperature Characteristics of RuO<sub>2</sub>-Based Thick Film Resistors

T. INOKUMA, Y. TAKETA and M. HARADOME, *Electro-component Sci. Technol.*, 1982, **9**, (3), 205-207

For some thick film resistors with conductive element RuO<sub>2</sub> and having almost zero TCRs, the electrical properties can be improved by doping with MnO<sub>2</sub>. These MnO<sub>2</sub> doped resistors have low TCR which is constant from low to high resistivity. The glass frits the resistors were made of was 52 PbO-35 SiO<sub>2</sub>-10 B<sub>2</sub>O<sub>3</sub>-3 Al<sub>2</sub>O<sub>3</sub> and RuO<sub>2</sub> was mixed into them in the ratio RuO<sub>2</sub>:glass 55:50, 25:75, 15:85 and 10:90, all measured in wt.-%.

## MEDICAL USES

### Synthesis and Antitumour Activity of Platinum Complexes Containing Neutral and Protonated Amine-Olefin Ligands

D. B. BROWN, A. R. KHOKHAR, M. P. HACKER, J. J. McCORMACK and W. M. STALICK, *Inorg. Chim. Acta, Bioinorganic Chem. Artic. Lett.*, 1982, **67**, (2), 45-52

A series of N-substituted allyl amines bound to Pt are reported. Under acidic conditions compounds of general formula (protonated amino-olefin) PtCl<sub>3</sub> are formed. All the complexes contain Pt-chloride bonds activated towards hydrolysis, and were examined for potential anti-tumour activity. Most of the protonated ligand complexes exhibited significant cytotoxicity against both *cis*-Pt sensitive and resistant L1210 leukaemia in cell culture.

## NEW PATENTS

### ELECTROCHEMISTRY

#### Electrolysis of Pure Water

CHLORINE ENGINEERS CORP. LTD.

*British Appl.* 2,094,835 A

Electrolysis of pure water may be carried out efficiently using a sulphonate group-containing cation exchange membrane between the anode and cathode compartments. Pt cathode catalysts and anodic catalysts of a platinum group metal or platinum group metal oxide are used in the cell.

#### Porous Catalytic Electrodes

INSTITUTE OF GAS TECHNOLOGY

*U.S. Patent* 4,328,287

Improved depolarisation and hence longer life is obtained for a catalytic gas flow electrode, for electrochemical and fuel cells, when a metastable colloid of electrochemically reducible or oxidisable gas bubbles is included in the electrolyte which flows through the electrode. O<sub>2</sub> in an electrolyte colloid flows through the Pt-catalysed O<sub>2</sub> electrode of an O<sub>2</sub>-Zn electrochemical cell.

### ELECTRODEPOSITION AND SURFACE COATINGS

#### Palladium-Nickel Alloy Electroplating Bath

LANGBEIN-PFANHAUSER WERKE A.B.

*British Appl.* 2,094,347/8 A

A plating bath which gives bright, grain-refined, Pd-Ni alloy deposits contains Pd and Ni in the form of amine salts, such as Pd(NH<sub>3</sub>)<sub>4</sub>SO<sub>4</sub> and Ni(NH<sub>3</sub>)<sub>6</sub>Cl<sub>2</sub> and acetylenealcohols, such as propargylalcohol, butanediol and hexenediol, as brighteners. In 2,094,348 A the brighteners used are acetylenic amines and/or an aminoalcohols in the form of a mixed crystal.

#### Ruthenium and Iridium Oxide Coatings on Semiconductors

M. GRAETZEL

*European Appl.* 57,669

The corrosion of CdS and other semiconductor electrodes exposed to light is reduced by a transparent coating of Ru and/or IrO<sub>2</sub>.