

# ABSTRACTS

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

### PROPERTIES

#### Experiment and Theory of 'Transparent' Metal Films

J. D. PORTER, A. HELLER and D. E. ASPNES, *Nature*, 1985, 313, (6004), 664-666

The optical properties of near-transparent porous Pt films supported on p-type InP are reported. The deposition of small quantities of catalytically active metals on p-InP increases the solar to H<sub>2</sub> conversion efficiency. Efficiencies increased slowly, even after fairly thick metallic layers had been deposited. The results imply that in certain conditions the metal overlayer is transparent to the incident light, or it even promotes the coupling of incident radiation into the bulk of the semiconductor. This is explained by the metal films being built up of particles smaller than the wavelength of the transmitted light, thus screening photons into the void structure which increases the effective refractive index of the layer.

#### Interaction of Gold with Platinum and Rhodium

E. M. SOKOLOVSKAYA, M. V. RAEVSKAYA, G. P. ZHMURKO, YU. D. SEROPEGIN and V. I. RODIONOV, *J. Less-Common Met.*, 1985, 105, (1), 161-164

Alloys of the Au-Pt-Rh system cast and tempered at 1000 and 1200°C were studied using a combination of physicochemical analysis methods. The results of the study enabled the boundaries of non-miscible liquid state components, sections at constant Au and Rh contents, and isothermal sections of the system at 1000 and 1200°C to be determined.

#### Properties of Platinum Yttrium-Boron Alloys

K. SCHWARZ and W. MOLLE, *Neue Huette*, 1984, 29, (11), 430-432

The properties of the alloy Pt-0.08Y were improved by the addition of B. At raised temperatures Pt-Y-B alloys in comparison to Pt-0.08Y alloy had higher stability with time, improved creep stability and reduced grain growth. Further, the B addition increased the rate of internal oxidation.

#### Spin Fluctuations and Superconductivity in UPt<sub>3</sub>

A. DE VISSER, J. J. M. FRANSE, A. MENOVSKY and T. T. M. PALSTRA, *J. Phys. F.*, 1984, 14, (9), L191-L196

Measurements of electrical resistivity, AC susceptibility and specific heat on Czochralski-grown single crystals of UPt<sub>3</sub> 6mm × 20mm reveal a transition into a superconducting state below 0.48K. From the experimental value of the upper critical field, an effective mass of 1.8m<sub>0</sub> is deduced. A numerical analysis of the normal state specific heat data below 20K is presented.

#### Electrical Conductivity and X-Ray Diffuse Scattering Study of the Family of Organic Conductors (perylene)<sub>2</sub>-M(mnt)<sub>2</sub>, (M = Pt, Pd, Au)

R. T. HENRIQUES, I. ALCÁCER, J. P. POUGET and D. JEROME, *J. Phys. C.*, 1984, 17, (29), 5197-5208

Resistivity measurements were made along the high conductivity axis of Per<sub>2</sub>Pt(mnt)<sub>2</sub>, Per<sub>2</sub>Pd(mnt)<sub>2</sub> and Per<sub>2</sub>Au(mnt)<sub>2</sub>. At low temperatures a clear metal-insulator phase transition is observed at 6.5 and 28K, respectively, for the first two salts, while it appears very gradually for the Au salt. The Pt and Pd salts above these critical temperatures have one-dimensional structural fluctuations, attributed to the M(mnt)<sub>2</sub> stacks. The diffuse scattering "condenses" in reflections below 28K in the Pd salt. The nature of the various phase transitions is discussed.

#### Heats of Adsorption of H<sub>2</sub> and CO on a Pd/TiO<sub>2</sub> "S.M.S.I." (Strong Metal-Support Interaction) Catalyst

A. VANNICE and P. CHOU, *J. Chem. Soc., Chem. Commun.*, 1984, (23), 1590-1591

The first measurement of heats of adsorption on a catalyst after it is in the SMSI state, obtained after a high temperature reduction in H<sub>2</sub>, is reported. CO and H<sub>2</sub> heats of adsorption on Pd/TiO<sub>2</sub> were comparable to or higher than those for typical Pd catalysts, indicating that suppressed chemisorption capacity in the SMSI state is not due to weakened adsorbate-metal bonds.

#### Separation and Concentration of Hydrogen Isotopes by Palladium-Alloy Membrane (I)

Y. SUZUKI and S. KIMURA, *J. At. Energy Soc. Jpn.*, 1984, 26, (9), 802-810

To find data on H isotope separation by Pd alloy membranes, permeabilities and solubilities of H and D were measured. The separation factor was affected by the boundary layer; values of boundary layer equations of velocities and concentrations were theoretically and experimentally found for various inlet velocities and He concentrations in the systems H<sub>2</sub>-He and D<sub>2</sub>-He.

#### The Ni-Pd (Nickel-Palladium) System

A. NASH and P. NASH, *Bull. Alloy Phase Diagrams*, 1984, 5, (5), 446-450

An assessed phase diagram of the Ni-Pd system is presented for temperatures from -200 to 1600°C. Data of crystal structure, lattice parameters, partial molar quantities, enthalpies, electronic specific heat and temperatures are given. The diagram is provisional and indicates a minimum melting point at 45at.%Pd.

### Kinetics and Mechanism of the Oxidation of Allyl Alcohol by Copper(II) Acetate in the Presence of Palladium(II) Chloride

I. AHMAD and C. ASHRAF, *Arab Gulf J. Sci. Res.*, 1984, **2**, (2), 417-423

A kinetic study of the oxidation of allyl alcohol by Cu(II) acetate in the presence of Pd(II) chloride is reported. The progress of the reaction was observed by measuring the disappearance of Cu(II) acetate concentration spectrophotometrically. The reaction is first order with respect to allyl alcohol and Pd(II) chloride, inverse first order with respect to  $(Cl^-)$  and zero order with respect to Cu(II) acetate. The rate is found to increase linearly with acetic acid concentration.

### Production of Ni-Pd-Si and Ni-Pd-P Amorphous Wires and Their Mechanical and Corrosion Properties

A. INOUE, Y. MASUMOTO, N. YANO, A. KAWASHIMA, K. HASHIMOTO and T. MASUMOTO, *J. Mater. Sci.*, 1985, **20**, (1), 97-104

Amorphous wires were made from 29-82 at.%Pd for (Ni-Pd)<sub>82</sub>Si<sub>18</sub> and 12-52 at.%Pd for (Ni-Pd)<sub>80</sub>P<sub>20</sub>. The wires were characterised by a circular cross-section and smooth surface. The wires had high mechanical strength, good ductility and corrosion resistance. As Ni content increased, tensile strength,  $\sigma_f$ , increased from 1340-1710 MPa and the elongation to fracture,  $\epsilon_f$ , decreased from 2.2% to 1.9%. Cold-drawing increased  $\sigma_f$  and  $\epsilon_f$  and smoothed the wire surface.

## CHEMICAL COMPOUNDS

### Synthesis, Structure and Antitumour Properties of Platinum Complexes of Vitamin C

L. S. HOLLIS, A. R. AMUNDSEN and E. W. STERN, *J. Am. Chem. Soc.*, 1985, **107**, (1), 274-276

A series of stable complexes of the form cis-[Pt(RNH<sub>2</sub>)<sub>2</sub>(ascorbate)] has been isolated and structurally characterised. The ascorbate ligand is bound to Pt in a unique fashion. Other Pt ascorbate chelates have been examined. These novel complexes of vitamin C are the first C-bound analogues of cis-diamineplatinum(II) to display good antitumour activity in vivo.

### Crystal Structure and Catalytic Properties of a Platinum-Iridium Mixed Cluster, [Pt<sub>2</sub>Ir<sub>2</sub>( $\mu$ -CO)<sub>3</sub>(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>3</sub>]

S. BHADURI, K. R. SHARMA, W. CLEGG, G. M. SHELDRICK and D. STALKE, *J. Chem. Soc., Dalton Trans.*, 1984, (12), 2851-2853

[Pt<sub>2</sub>Ir<sub>2</sub>(CO)<sub>7</sub>(PPh<sub>3</sub>)<sub>3</sub>] has been synthesised from [Pt<sub>12</sub>(CO)<sub>24</sub>]<sup>2-</sup> and [Ir(CO)Cl(PPh<sub>3</sub>)<sub>2</sub>], and characterised. The metal atoms adopt a butterfly configuration with the Ir and Pt atoms occupying the "hinge" and "wing-tip" positions, respectively. The mixed metal cluster is an active catalyst for hydrogenation of olefins.

### Cobalt, Rhodium and Iridium, Annual Survey Covering the Year 1983

J. T. MAGUE, *J. Organomet. Chem.*, 1984, **278**, (1-3), 1-204

A review of organic Rh, Ir and Co complexes and compounds is presented. Complexes discussed include metal-C  $\sigma$ -bonded, metal carbene, metal isocyanide, metal carbonyls, nitrosyls and arylidiazos, alkenes, alkynes,  $\pi$ -allyls, carbocyclics, metallaborane and -carbaborane, and several miscellaneous complexes. (808 Refs.)

### Chiral Discrimination in the Covalent Binding of Bis(phenanthroline)-dichlororuthenium(II) to B-DNA

J. K. BARTON and E. COLIS, *J. Am. Chem. Soc.*, 1985, **107**, (3), 708-709

Bis(1,10-phenanthroline)dichlororuthenium(II) was found to bind covalently to the DNA duplex and exhibited striking enantiomeric selectivity, different from that seen on intercalation, which may have significant biological consequences for chemotherapeutic application.

### Convenient Syntheses of Bis(2,2'-bipyridine) Complexes of Ru(III)

F. BOTTOMLEY and M. MUKAIDA, *Inorg. Chim. Acta, Artic. Lett.*, 1985, **97**, (2), L29-L30

A one-pot synthesis of [RuCl<sub>2</sub>(bipy)<sub>2</sub>]<sup>+</sup> and its single step conversion into [(RuX(bipy)<sub>2</sub>]<sub>2</sub>( $\mu$ -O)]<sup>2+</sup> are given.

## ELECTROCHEMISTRY

### Electrochemical Preparation and Characteristics of Platinum Electrode Surfaces with Preferred Orientations

R. M. CERVINO, W. E. TRIACA and A. J. ARVIA, *J. Electroanal. Chem. Interfacial Electrochem.*, 1985, **182**, (1), 51-60

A new electrochemical procedure for obtaining Pt electrode surfaces with preferred orientations from bulk polycrystalline Pt is presented. The procedure involves repetitive potential sweeps at high frequencies on a polycrystalline Pt electrode under potential perturbation conditions.

### Electrocatalytic Activity of Platinum, Rhodium, Iridium and Their Alloys in Oxidising Synthesis at High Positive Potentials

YA. M. KOLOTYRKIN, A. A. YAKOVLEVA and I. I. KUVINOVA, *J. Electroanal. Chem. Interfacial Electrochem.*, 1984, **180**, (1 & 2), 241-256

The electrocatalytic activities of Pt, Rh, Ir, Pt-Rh and Pt-Ir anodes were compared during formation of the peroxodisulphate ion, S<sub>2</sub>O<sub>8</sub><sup>2-</sup>. The mechanisms of the process and the effect of adsorption layers on the selectivity were examined. Alloys with low Rh or Ir content (up to 10%) had greater activity and selectivity than Pt due to changes in adsorption properties of the oxide film on the Pt, when doped with small quantities of Rh or Ir.

### A Selective Catalyst for Titanium Anodes: Development and Optimization. I. Catalyst Structure, Activity and Durability. II. Selectivity Features

N. KRSTAJIĆ, M. SPASOJEVIĆ and M. JAKŠIĆ; M. SPASOJEVIĆ, N. KRSTAJIĆ and M. JAKŠIĆ, *J. Res. Inst. Catal., Hokkaido Univ.*, 1984, **32**, (1), 19–28; 29–36

A composite electrocatalytic coating of RuO<sub>2</sub>/TiO<sub>2</sub> and PdSn<sub>2</sub> with improved anionic features for sea water electrolysis and chlorate cells has been developed, for Cl<sub>2</sub> evolution. The coating is intended for use where O<sub>2</sub> evolution is undesirable. An optimised composition of 14at.%Ru, 35at.%Ti, 17at.%Pd and 34at.%Sn has shown high activity for Cl<sub>2</sub> evolution, good corrosion resistance and low activity for O<sub>2</sub> evolution. The high selectivity comes from high O overpotential and from its adsorption behaviour.

### Oxygen Reduction on Ruthenium Electrodes Modified by Foreign Metal Adsorbates

R. R. ADŽIĆ, N. A. ANASTASIJEVIĆ and S. M. DIMITRIJEVIĆ, *J. Electrochem. Soc.*, 1984, **131**, (11), 2730–2731

A completely inactive surface of oxidised Ru was modified by Th and Pb adsorbates so that the surface showed a pronounced activity for O<sub>2</sub> reduction.

### Electrochemical Behavior of Ru(trpy)(bpy)(OH<sub>2</sub>)<sup>3+</sup> in Aqueous Solution and when Incorporated in Nafion Coatings

R. C. McHATTON and F. C. ANSON, *Inorg. Chem.*, 1984, **23**, (24), 3935–3942

The rate at which the title Ru(II) complex is electrooxidised is controlled by the kinetics of a chemical step that precedes the electrode reaction. It is proposed that the oxidation rate is limited by the rate of pH-dependent ligand exchange reactions in which a Ru-N bond is broken. Graphite electrodes coated with Nafion incorporating the Ru(II) complex exhibit high catalytic activity toward the electrooxidation of benzyl alcohol. Catalyst activity can be restored after degradation.

## PHOTOCONVERSION

### Photocatalytic Reactions of Azide Ions on Platinized Titanium Dioxide Powders in Solutions

Y. NOSAKA, Y. ISHIZUKA, K. NORIMATSU and H. MIYAMA, *Bull. Chem. Soc. Jpn.*, 1984, **57**, (11), 3066–3069

NH<sub>3</sub> was photocatalytically produced from an aqueous solution of azide ion by illuminating Pt/TiO<sub>2</sub> semiconductor powder. Other reaction products of N<sub>2</sub> and small amounts of N<sub>2</sub>O and NO<sup>-</sup> were also detected. H<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub>H<sub>4</sub> were not formed in the primary reaction products. The illuminated Pt/TiO<sub>2</sub> powder appears to act as a microelectrode.

### H<sub>2</sub> Photoproduction by Nafion/CdS/Pt Films in H<sub>2</sub>O/S<sup>2-</sup> Solutions

A. W.-H. MAU, C.-B. HUANG, N. KAKUTA, A. J. BARD, A. CAMPION, M. A. FOX, J. M. WHITE and S. E. WEBBER, *J. Am. Chem. Soc.*, 1984, **106**, (22), 6537–6542

The construction, characterisation and evaluation of a novel system for photocatalytic H<sub>2</sub> generation that comprises semiconductor CdS crystallites embedded in a polymer Nafion matrix which also contains a H<sub>2</sub>-evolution Pt catalyst is reported. H<sub>2</sub>-production efficiencies from H<sub>2</sub>O containing a sacrificial electron donor were greater than those commonly obtained with unsupported colloidal or powdered semiconductors.

### Basic Problems of Photochemical and Photoelectrochemical Hydrogen Production from Water

N. GETOFF, *Int. J. Hydrogen Energy*, 1984, **9**, (12), 997–1004

Some basic problems in photochemical and photoelectrochemical H<sub>2</sub> and/or O<sub>2</sub> production in hybrid, homogeneous and heterogeneous water splitting systems by solar energy are discussed. Among systems examined are those with metal-organic complexes, such as Ru(bipy)<sub>3</sub><sup>2+</sup> and MV<sup>2+</sup>, coupled with redox catalysts, such as RuO<sub>2</sub> and colloidal Pt, photogalvanic cells, liquid-junction transducers and photochemical systems, including those with multifunctional solid catalysts and semiconductor dispersions and colloids.

### Electron-Transfer Reaction and Formation of Active Species Induced by Both Applied Potential and Photoexcitation

M. KANEKO, A. YAMADA and N. OYAMA, *Nippon Kagaku Kaishi*, 1984, (11), 1810–1814

Electron-transfer reactions and formation of active species induced by both applied potential and photoexcitation were studied. A graphite electrode coated with Nafion membrane and then [Ru(bpy)<sub>3</sub><sup>2+</sup>] was adsorbed into the polymer layer. The modified electrode was illuminated with visible light in the presence of MV<sup>2+</sup> to give cathodic or anodic photocurrent, depending on the applied potential. The cathodic photocurrent brought about formation of viologen cation radical (MV<sup>•+</sup>). The cathodic photocurrent was enhanced ~9 times in the presence of O<sub>2</sub> due to oxidation of MV<sup>•+</sup>.

### Photochemical Reduction of Carbon to Formate Mediated by Ruthenium Bipyridine Complexes as Homogeneous Catalysts

J. HAWECKER, J.-M. LEHN and R. ZIESSEL, *J. Chem. Soc., Chem. Commun.*, 1985, (2), 56–58

Visible light irradiation of Ru(bipy)<sub>3</sub>Cl<sub>2</sub> in dimethylformamide-triethanolamine medium containing CO<sub>2</sub>, leads to efficient and preferential reduction of the CO<sub>2</sub> to formate.

## Photocatalysed Reactions on Clay Surfaces

H. VAN DAMME, H. NIJS and J. J. FRIPIAT, *J. Mol. Catal.*, 1985, 27, (1-2), 123-142

A review of recent work on the photochemical and photocatalytic properties of co-ordination compounds adsorbed within the intracrystal space of smectites or on the external surface of fibrous clays is presented. Reactions examined include the cis-trans isomerisation of  $[\text{Ru}(\text{II})(\text{bpy})_2(\text{H}_2\text{O})_2]^{2+}$ , the photoaquation of  $\text{Ru}(\text{II})(\text{bpy})_3^{3+}$  and  $\text{Cr}(\text{III})(\text{bpy})_3^{3+}$  and in addition the photooxidation of  $\text{H}_2\text{O}$  using cis- $[\text{Ru}(\text{II})(\text{bpy})_2(\text{H}_2\text{O})_2]^{2+}$  as a catalyst. (23 Refs.)

## LABORATORY APPARATUS AND TECHNIQUE

### Amperometric Gas Sensor Using Solid State Proton Conductor Sensitive to Hydrogen in Air at Room Temperature

N. MIURA, H. KATO, Y. OZAWA, N. YAMAZOE and T. SEIYAMA, *Chem. Lett. Jpn.*, 1984, (11), 1905-1908

A new type of amperometric gas sensor, using a proton conductor (antimononic acid), and its working mechanism are examined for detecting small amounts of  $\text{H}_2$  in air at room temperature. The sensor element is air, Pt black counter electrode | proton conductor membrane | Pt black sensing electrode for the sample gas. The sensor electrode was modified by coating it with teflon and epoxy resin. This modified sensor had excellent  $\text{H}_2$  response.

### A Stable Pd-BN-Si<sub>3</sub>N<sub>4</sub>-SiO<sub>2</sub>-Si FET for Hydrogen Detection

W. TORBICZ, D. SOBCZYNSKA, A. OLSZYNA, G. FORTUNATO and A. D'AMICO, *Phys. Status Solidi A*, 1984, 86, (1), 453-459

$\text{H}_2$  sensitive Pd-gate MISFET structures were fabricated using insulating multilayers to avoid the instability problems associated with the  $\text{SiO}_2$ -H interaction in Pd-SiO<sub>2</sub> semiconductor devices. The use of BN is proposed for the first time as a fundamental part of the insulating multilayers. Several multilayers were tested as insulators in Pd-gate MIS devices. The best performances were obtained with the Pd-BN-Si<sub>3</sub>N<sub>4</sub>-SiO<sub>2</sub>-Si structure.

## HETEROGENEOUS CATALYSIS

### Propane Conversion to Aromatic Hydrocarbons on Pt/H-ZSM-5 Catalysts

T. INUI and F. OKAZUMI, *J. Catal.*, 1985, 90, (2), 366-367

A novel catalyst was developed for the selective conversion of propane to liquid fuel or aromatic compounds. The catalyst was made from Pt/H-ZSM-5. Various catalysts were tested, and the temperature distribution of the products noted. A major part of the products heavier than  $\text{C}_3$  hydrocarbons were aromatics at temperatures  $>400^\circ\text{C}$ , most of the hydrocarbons with  $\text{C} < 3$  were  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$ .

## Surface Structure and Composition Changes on Platinum-Rhodium Alloy Catalysts

A. R. McCABE and G. D. W. SMITH, *J. Phys., Colloq. 9, Suppl. 12*, 45, 1984, C9-483-C9-488

Pt-Rh gauze catalysts used in the manufacture of  $\text{HNO}_3$  acid undergo an extensive surface reconstruction process. This has been investigated in a miniature catalytic reactor by various techniques. A mechanism involving vapour transport is proposed to explain the main features in the variation in catalytic behaviour with operating conditions.

## CO Methanation Activity and XPS Studies of Pd Supported on ZSM5 and Y-Zeolites

N. C. SAHA and E. E. WOLF, *Appl. Catal.*, 1984, 13, (1), 101-112

The hydrogenation of CO has been studied on a series of Pd catalysts supported on H-ZSM5, Na-ZSM5, H-Y, Na-Y zeolites and  $\text{SiO}_2$ , at atmospheric pressure and  $300$ - $550^\circ\text{C}$ .  $\text{CH}_4$  and  $\text{H}_2\text{O}$  were the main products. Methanation activity decreased in the order  $\text{H-Y} > \text{H-ZSM5} > \text{Na-ZSM5} \gg \text{Na-Y} > \text{SiO}_2$ , showing that support acidity affects the activity. Pd on ZSM5 (H, Na) zeolites had remarkable stability for deactivation even at  $500^\circ\text{C}$ , while irreversible deactivation occurred on Pd/Y-zeolite and Pd/SiO<sub>2</sub>. Pd was the predominant active species. C causes deactivation only at temperatures  $>400^\circ\text{C}$ .

## Colloidal Catalyst Coated Semiconductors in Surfactant Vesicles. In Situ Generation of Rhodium-Coated Sulfide Particles in Dioctadecyldimethylammonium Halide Surfactant Vesicles and Their Utilization in Photosensitized Charge Separation and Hydrogen Generation

R. RAFAELOFF, Y.-M. TRICOT, F. NOME and J. H. FENDLER, *J. Phys. Chem.*, 1985, 89, (3), 533-537

Colloidal  $\sim 40\text{\AA}$  diameter CdS semiconductors were generated in situ and coated in situ by Rh in  $800$ - $1000\text{\AA}$  diameter DODA chloride and DODA bromide surfactant vesicles. Vesicles controlled the sizes and stabilities of CdS, generated by  $\text{H}_2\text{S}$  from adsorbed Cd/EDTA. Catalyst coating was achieved by visible light irradiation in the presence of a suitable electron donor.

## Direct Synthesis of Acetic Acid from Synthesis Gas

U. DETTMEIER, E. I. LEUPOLD, H. PÖLL, H.-J. SCHMIDT and J. SCHÜTZ, *Erdoel Kohle Erdgas Petrochem.*, 1985, 38, (2), 59-62

A gas phase process using supported Rh catalysts has been developed to produce O-containing  $\text{C}_2$ -compounds (acetic acid, acetaldehyde, ethanol and ethylacetate) directly from synthesis gas, with selectivities up to 80%.  $\text{CH}_3\text{COOH}$  is the main product after an oxidative work-up followed by fractional distillation. A process was designed for manufacturing acetic acid by this method and production costs were estimated.

## The Water Gas Shift Reaction Catalysed by Rh<sub>6</sub>(CO)<sub>16</sub> Adsorbed on Alumina or [Rh(CO)<sub>2</sub>Cl]<sub>2</sub> Adsorbed on Alumina, Na-Y Zeolite and H-Y Zeolite

J. M. BASSET, A. THEOLIER, D. COMMEREUC and Y. CHAUVIN, *J. Organomet. Chem.*, 1985, **279**, (1/2), 147-158

Rh<sub>6</sub>(CO)<sub>16</sub> chemisorbed on  $\eta$ -Al<sub>2</sub>O<sub>3</sub>, or [Rh(CO)<sub>2</sub>Cl]<sub>2</sub> chemisorbed on  $\eta$ -Al<sub>2</sub>O<sub>3</sub>, Na-Y zeolite and H-Y zeolite catalyse the water gas shift reaction with the order of activity Al<sub>2</sub>O<sub>3</sub> > Na-Y > H-Y. With Al<sub>2</sub>O<sub>3</sub> the reaction occurs between 25 and 100°C. Turnover numbers as high as 255/Rh atom/hour are obtained at 50°C and under 50 atm. The reaction mechanism was deduced and involves three steps. If the CO pressure is too low or if liquid water is used, ageing of the catalyst occurs, which seems to be due to formation of metallic Rh.

## Novel Rh/TiO<sub>2</sub> and Ir/TiO<sub>2</sub> Catalysts for n-Butane Isomerization and Dehydrogenation

D. E. RESASCO and G. L. HALLER, *J. Phys. Chem.*, 1984, **88**, (20), 4552-4556

An ion-exchange preparation of TiO<sub>2</sub>-supported Rh and Ir which produces a 100% dispersed, low metal loading (0.3%) catalyst is described. When these catalysts are reduced at ~773K, they exhibit a unique activity for alkane isomerisation and dehydrogenation. Hydrogenolysis has an unusual positive order in H and a relatively high selectivity for terminal vs. central C-C bond breaking in n-butane for these catalysts compared to impregnated Rh and Ir catalysts. This behaviour may be the result of the SMSI which results in a change in the mechanism of hydrogenolysis to one where alkane isomerisation competes with hydrogenolysis.

## Selective Synthesis of C<sub>2</sub>-Oxygenated Compounds from Synthesis Gas over Ir-Ru Bimetallic Catalysts

H. HAMADA, Y. KUWAHARA, Y. KINTAICHI, T. ITO, K. WAKABAYASHI, H. IJIMA and K.-I. SANO, *Chem. Lett. Jpn.*, 1984, (9), 1611-1612

Ir-Ru/SiO<sub>2</sub> bimetallic catalysts produced C<sub>2</sub>-oxygenated compounds from synthesis gas at temperatures from 280-300°C under 50 atm. Adding Li to the bimetallic catalyst improved the catalytic activity and selectivity.

## Effects of Additives on the Selectivity in Fischer-Tropsch Synthesis by Alumina-Supported Ruthenium Catalysts

T. OKUHARA, T. ENOMOTO, H. TAMURA and M. MISONO, *Chem. Lett. Jpn.*, 1984, (9), 1491-1494

Addition of K and P to Ru/Al<sub>2</sub>O<sub>3</sub> changed the selectivity of Fischer-Tropsch synthesis by affecting mainly the electronic state of Ru. K addition increased the olefin:paraffin ratio and decreased the CH<sub>4</sub> formation. The effect of P was the opposite. However, adding V suppressed CH<sub>4</sub> formation with only a slight decrease in the olefin:paraffin ratio.

## HOMOGENEOUS CATALYSIS

### Gas-Phase Platinum Cluster Reactions with Benzene and Several Hexanes. Evidence of Extensive Dehydrogenation and Size-Dependent Chemisorption

D. J. TREVOR, R. L. WHETTON, D. M. COX and A. KALDOR, *J. Am. Chem. Soc.*, 1985, **107**, (2), 518-519

The chemisorption of hydrocarbons, benzene, cyclohexane, 2,3-dimethylbutane and n-hexane and their dehydrogenation were examined on unsupported Pt metal clusters. The gas-phase Pt clusters were found to dehydrogenate saturated hydrocarbons to a C:H ratio  $\approx$ 1, and exhibited cluster-size-dependence on chemisorption.

### Inclusion of Metallic Aggregates in Organic Conducting Polymers. A New Catalytic System [Poly(3-methylthiophene)-Ag-Pt], for Proton Electrochemical Reduction

G. TOURILLON and F. GARNIER, *J. Phys. Chem.*, 1984, **88**, (22), 5281-5285

The [poly(3-methylthiophene)-Ag-Pt] catalytic system was shown to have a very high catalytic activity for proton electrochemical reduction, with a current density of 200mA/cm<sup>2</sup> and remarkable stability for more than 170h when compared to the corresponding [polypyrrole-Ag-Pt] catalytic system.

### Linear Dimerization of Acrylates by Palladium and Rhodium Catalysts. Effect of Lewis and Protic Acid Additives

W. A. NUGENT and R. J. MCKINNEY, *J. Mol. Catal.*, 1985, **29**, (1), 65-76

The rates of catalytic dimerisation of alkyl acrylates by PdCl<sub>2</sub>(NCPH)<sub>2</sub> and by [(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>RhCl]<sub>2</sub> are greatly increased by the combination of a Lewis acid promoter and a proton source. For the Rh systems, catalyst life was also enhanced and yields of up to 280mol/mol Rh with >98% selectivity to linear dialkyl hexenedioates have been observed. Optimal conditions needed [(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>RhCl]<sub>2</sub>, FeCl<sub>3</sub> and methanol in the proportions 1:5:10 at 80°C. Catalyst and promoter combination markedly influenced the isomeric composition of the production.

### Preparation of New Peralkyldiphosphines as Efficient Ligands for Catalytic Asymmetric Hydrogenation of $\alpha$ -Dicarbonyl Compounds

K. TANI, T. ISE, Y. TATSUNO and T. SAITO, *J. Chem. Soc., Chem. Commun.*, 1984, (24), 1641-1643

New chiral peralkyldiphosphines (1) containing a pyrrolidine ring have been prepared by a new method which is widely applicable to transform known chiral diphosphines into the corresponding cyclohexyl analogues. The asymmetric hydrogenation of  $\alpha$ -dicarbonyl compounds catalysed by Rh complexes of (1) proceeds smoothly under mild conditions (1atm H<sub>2</sub> and 35°C), to give moderate optical yields.

## Iridium Complexes as Hydrosilylation Catalysts

D. C. APPLE, K. A. BRADY, J. M. CHANCE, N. E. HEARD and T. A. NILE, *J. Mol. Catal.*, 1985, **29**, (1), 55-64

Ir complexes are active as catalysts for hydrosilylation reactions, especially those involving 1,3-dienes and 1-alkynes. For ketones, Ir complexes show maximum activity if one molar equivalent of triphenylphosphine is added to the reaction mixture. Ir complexes are also active catalysts for the hydrosilylation of  $\alpha,\beta$ -unsaturated ketones.

## FUEL CELLS

### Fuel Cells: Principles and Prospects

G. PRENTICE, *Chemtech*, 1984, (11), 684-694

A review of the history, theory and current research on fuel cell technology is presented. Electrode materials, fuels, electrolytes, operating conditions and adapting fuel cells for various uses are examined. The efficiencies, cost factors, phosphoric and acid fuel cells, the use of Pt<sub>3</sub>V, molten carbonate fuel cells and future developments are also reviewed.

### Polarization at Pt Electrodes of a Fuel Cell with a High Temperature-Type Proton Conductive Solid Electrolyte

H. UCHIDA, S. TANAKA and H. IWAHARA, *J. Appl. Electrochem.*, 1985, **15**, (1), 93-97

Polarisation phenomena in the Pt electrodes of a proton conducting fuel cell with SrCe<sub>0.95</sub>Yb<sub>0.05</sub>O<sub>3- $\alpha$</sub>  as the solid electrolyte,  $\alpha$  being the number of O deficiencies per perovskite-type oxide unit cell, were investigated by a current interruption method. The polarisation of the cathode could not be neglected below 900°C, whereas the polarisation of the anode was negligibly small. The polarisation resistance at the cathode decreased with increasing O partial pressure. The rate determining step for the cathode reaction was the surface diffusion of adsorbed O atoms on Pt to the active site on the electrolyte.

## NEW PATENTS

### METALS AND ALLOYS

#### Ruthenium Alloy

TOKYO SHIBAURA DENKI K.K. U.S. Patent 4,464,208

An amorphous alloy for a magnetic head contains, in specified proportions, Ru, Co, Fe, Si, B, and at least one of Ti, V, Cr, Mn, Ni, Zr, Nb, Mo, Hf, Ta and W.

#### Permanent Magnet Alloy

RESEARCH INSTITUTE OF ELECTRIC & MAGNETIC ALLOYS U.S. Patent 4,465,526

An easily workable alloy for permanent magnets of high coercive force has a crystalline structure with a fine grain dispersion of alpha phase and gamma phase in a matrix. It contains 19.5-41 at.% Pd, 0.1-27.5 at.% Ag, remainder Fe.

### Application of the Gas Diffusion Electrode of High Performance to Methanol Fuel Cells

N. FURUYA and S. MOTOO, *J. Electroanal. Chem. Interfacial Electrochem.*, 1984, **179**, (1 & 2), 303-306

The application of a gas diffusion electrode of high performance to methanol oxidation in the methanol fuel cell resulted in high current densities of 0.25A/cm<sup>2</sup> at 0.42V, 0.50A/cm<sup>2</sup> at 0.45V and 1A/cm<sup>2</sup> at 0.520mV at 70°C. The counter electrode was a Pt mesh and the electrocatalyst was a Pt + Ru system of varying composition, the loading varying from 0 to 5mg/cm<sup>2</sup>.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### New Thick Film Capacitor Dielectrics

S. J. STEIN, C. HUANG and P. BLESS, *Solid State Technol.*, 1984, **27**, (10), 213-219

A new series of thick film dielectrics for firing at 850-1000°C has been developed from experiments involving Pt/Au, Pd/Au and Au. Dielectric constant nominal values of 25, 50 and 100, respectively, were achieved. The dielectrics had low temperature coefficients of capacitance, Q values >100, high insulation resistance and good stability to thermal, voltage and humidity stresses with Pd/Ag electrodes.

### Performance of Pairs of Hafnium and Rhodium Self-Powered in-Core Detectors in a Pressurized Water Reactor

H. D. WARREN, C. T. ROMBOUGH, T. G. PITTS and M. L. GILBERT, *Nucl. Sci. Eng.*, 1984, **88**, (4), 486-494

Two assemblies of self-powdered in-core detectors have been tested in a pressurised water reactor for over one year. The assemblies contain both prompt responding Hf and delayed-responding Rh detectors. 4 Hf detectors were paired with 4 Rh detectors in each assembly. The Rh detectors were used to calibrate the Hf detectors on line.

### Platinum Group Metals in Hydrogen Storage Materials

STUDIENGESELLSCHAFT KOHLE m.b.H.

*German Offen.* 3,247,360

A useful H storage material is made by doping Mg hydride with a transition metal which may be Pt, Pd, Rh or Ir, among others.

## ELECTROCHEMISTRY

### Semiconductor Electrode

FUJITSU LTD. *European Appl.* 127,281

An electrode has a three layer structure consisting of a contact layer (such as Pt silicide), an intermediate refractory layer and a surface layer (of Pt, Au, etc.).