

# ABSTRACTS

of current literature on the platinum metals and their alloys

## PROPERTIES

### X-Ray Photoelectron Diffraction Study of Platinum Particles Deposited on Rutile Titanium Dioxide

K. TAMURA, U. BARDI and Y. NIHEI, *Surf. Sci.*, 1989, **216**, (1/2), 209-221

X-ray photoelectron diffraction (XPED) has been used to study Pt deposited by thermal evaporation in vacuum on the (110), (100) and (001) surfaces of rutile TiO<sub>2</sub> single crystals. For the (110) and (100) surfaces, after Pt deposition and annealing, an intense modulation of the photoelectron intensity as a function of the emission angle was observed from the Pt overlayer. Analysis of these results showed that most of the Pt clusters grew epitaxially with the (111) plane parallel to the substrate surface. Complete structural analysis could not be performed for the (001) oriented substrate.

### Effects of the Film Thickness on the Interfacial Reaction of Pt/(111)Si

J.-R. CHEN, L.-D. CHANG and F.-S. YEH, *J. Vac. Sci. Technol.*, 1989, **A7**, (3), 1345-1349

Transmission electron diffraction and X-ray diffraction have been used to study the effect of Pt thin film thickness (50-300Å) on silicide formation and microstructure when Pt was deposited onto p-type, (111)-oriented Si substrates, kept at 450°C.  $\beta$ -Pt<sub>2</sub>Si was observed in samples with 50 and 200Å thick Pt films, but with different orientations. As-deposited samples with 300Å Pt showed the formation of PtSi epitaxial layer, Pt polycrystalline, and the texture polycrystalline of  $\alpha$ -Pt<sub>2</sub>Si.

### Hydrogen Chloride Adsorption and Co-adsorption with Hydrogen or Water on Platinum (111)

F. T. WAGNER and T. E. MOYLAN, *Surf. Sci.*, 1989, **216**, (3), 361-385

Aqueous Cl<sup>-</sup> ions accelerate the corrosion of all metals, and Cl<sup>-</sup> chemistry is essential to the preparation of platinum metal catalysts. The adsorption of anhydrous HCl on Pt(111) at 90K and its coadsorption with H and H<sub>2</sub>O have been studied by various analytical techniques in order to determine the interaction of Cl<sup>-</sup> species with metals. The chemistry of HCl adsorption and coadsorption on Pt(111) is dominated by strong Pt-Cl interactions. Low coverages of HCl fully dissociate on Pt(111) at 90K to form disordered adsorbed H and Cl. Higher exposures produced first a well-ordered 3×3 phase and then an increasingly disordered form, again of adsorbed H and Cl. Coadsorption of HCl+H<sub>2</sub>O produced adsorbed H<sub>2</sub>O<sup>+</sup>.

### Thermal Reaction between Pt Thin Films and Si<sub>x</sub>Ge<sub>1-x</sub> Alloys

Q. Z. HONG and J. W. MAYER, *J. Appl. Phys.*, 1989, **66**, (2), 611-615

Thermal reaction of Pt with amorphous Si<sub>x</sub>Ge<sub>1-x</sub> alloys (x=0.25-0.75) was studied at 200-650°C. At low temperatures of 200-400°C, a uniform reacted layer containing a mixture of Pt<sub>2</sub>Si and Pt<sub>2</sub>Ge was produced. The formation of these phases was diffusion controlled with a measured activation energy of 1.2 eV for all the Si<sub>x</sub>Ge<sub>1-x</sub> alloys. Reaction continued with the formation of monosilicide and monogermanide. At high temperatures of 400-650°C, phase separation occurred in depth with a surface layer enriched with Si and a bottom layer enriched with Ge. The formation of PtGe<sub>2</sub> and the crystallisation of unreacted amorphous Si<sub>x</sub>Ge<sub>1-x</sub> were observed.

### D<sub>2</sub> on Pd(110): Surface and Subsurface Phases, Absolute Coverages, and Interconversion

U. MEMMERT, J.-W. HE, K. GRIFFITHS, W. N. LENNARD, P. R. NORTON, N. V. RICHARDSON, T. E. JACKMAN and W. N. UNERTL, *J. Vac. Sci. Technol.*, 1989, **A7**, (3), 2152-2154

Adsorption of D<sub>2</sub> on Pd(110) at low temperature produced (2×1) and (1×2) phases in sequence. Rutherford backscattering data showed that the (2×1) structure was unreconstructed, while the (1×2) was reconstructed, with an entire monolayer (ML) of Pd atoms displaced laterally from their bulklike locations by ≥0.01nm. Nuclear reaction analysis data demonstrated that depending on the method of preparation, the (2×1) phase can be associated with a total coverage of 1 or 1.5ML, while the (1×2) phase can be produced with total coverages of 1.5 or 2ML. The additional 0.5ML, associated with the high coverage of each phase, was due to subsurface adsorbed species.

### Surface Phenomena and Isotope Effects at Low Temperature Palladium Hydride Formation and during Its Decomposition

R. DUŚ, E. NOWICKA and Z. WOLFRAM, *Surf. Sci.*, 1989, **216**, (1/2), 1-13

Adsorption states of H and D, arising in the process of low temperature (78K) Pd hydride (deuteride) formation in thin Pd films were distinguished by simultaneous surface potential and pressure measurements. The precursor state for H (D) incorporation into the bulk was determined, and the diffusion coefficients calculated to be (2-4)×10<sup>-13</sup>cm<sup>2</sup>/s for H and (0.7-1.5)×10<sup>-13</sup>cm<sup>2</sup>/s for D. Surface potential isotherms were obtained for Pd hydride (deuteride) and showed a significant isotope effect.

## The Effect of Adsorbed Carbon and Sulphur on Hydrogen Permeation through Palladium

A. B. ANTONIAZZI, A. A. HAASZ and P. C. STANGEBY, *J. Nucl. Mater.*, 1989, **162-164**, 1065-1070

In experiments performed with upstream  $H_2$  pressures of  $\sim 10^{-3}$ -300 Pa and at 355-630 K the permeation rate of  $H_2$  through Pd, on which C or S is adsorbed, varied by a factor of  $\sim 10^4$ . The H recombination coefficient,  $K_r$ , derived from permeation data, increased by a factor of  $\sim 10^3$  when the C coverage was reduced from 0.36 to 0.06 at  $T=600$  K. A S coverage decrease from 0.14 to 0.06 increased  $K_r$  ( $T=625$  K) by a factor of  $\sim 4$ .

## Thermal Stability of the C-O Bond of Methanol on the Pd(111) Surface: An Isotopic Mixing Study

X. GUO, L. HANLEY and J. T. YATES, *J. Am. Chem. Soc.*, 1989, **111**, (9), 3155-3157

The thermal desorption of CO molecules produced from methanol decomposition on Pd(111) has been studied by isotopic mixing. Using  $^{13}CH_3^{16}OH$  and  $^{12}CH_3^{18}OH$  adsorbate molecules, no isotopic exchange in thermally desorbing CO to produce  $^{13}C^{18}O$  and  $^{12}C^{16}O$  was observed. Along with studies showing that no  $H_2O$  or  $CH_4$  desorbs, this observation indicates that C-O bond scission does not occur in any of the surface species derived from methanol.

## Unusual Kinetics of Hydride Formation in Mg-Pd Sandwiches, Studied by Hydrogen Profiling and Quartz Crystal Microbalance Measurements

J. RYDÉN, B. HJÖRVARSSON, T. ERICSSON, E. KARLSSON, A. KROZER and B. KASEMO, *J. Less-Common Met.*, 1989, **152**, (2), 295-309

Hydrogen uptake by Pd-covered Mg samples of Mg thicknesses of 600-1,300 nm with Pd coating of 7-8 nm, was studied at 260-403 K and at pressures of 0.03-30 Torr by depth profiling and quartz crystal microbalance measurements. The unusual pressure dependence observed for the H uptake which increased with decreasing pressure, is related to the formation of a hydride in the Mg near the Pd-Mg interface. The uptake was kinetically restricted at  $\sim 296$  K and pressures of  $\geq 0.01$  Torr.

## Diffusion of Silicon in Pd<sub>2</sub>Si during Growth

C. M. COMRIE and J. M. EGAN, *J. Vac. Sci. Technol.*, 1989, **A7**, (3), 1492-1496

Radioactive  $^{31}Si$  has been used to study the diffusion of Si in Pd<sub>2</sub>Si during silicide formation. Results show that Si diffuses by a vacancy mechanism during polycrystalline Pd<sub>2</sub>Si growth, and that Si self-diffusion is relatively small in completely formed Pd<sub>2</sub>Si but is extremely large during silicide growth. The most likely mechanism of Si diffusion in epitaxial Pd<sub>2</sub>Si is also a vacancy mechanism. Pd does not diffuse through epitaxial Pd<sub>2</sub>Si during silicide growth.

## Spillover Effects in the Detection of H<sub>2</sub> and CH<sub>4</sub> by Sputtered SnO<sub>2</sub> Films with Pd and PdO Deposits

R. HUCK, U. BÖTTGER, D. KOHL and G. HEILAND, *Sens. Actuators*, 1989, **17**, (3&4), 355-359

Auger spectroscopy has been used to study the deposition of up to 10 monolayers (ML) of Pd on SnO<sub>2</sub>(110) crystal faces in UHV. Initial layer-by-layer growth was followed by cluster formation. O from the substrate was transferred to the clusters and metallic Sn was observed. After annealing at  $>650^\circ C$  in UHV, SnO<sub>2</sub> reappeared, indicating a strong metal-support interaction. Sputtered SnO<sub>2</sub> films with an 8 ML Pd deposit showed an open substrate surface besides Pd clusters. Spillover effects are discussed to explain the increase in conductance in air containing H<sub>2</sub> or CH<sub>4</sub> of films with Pd and PdO clusters compared to those without Pd clusters.

## Solubility of Hydrogen in Pd<sub>2</sub>Er<sub>5</sub>, Pd<sub>2</sub>Er<sub>3</sub>, PdEr, Pd<sub>4</sub>Er<sub>3</sub>, and Pd<sub>3</sub>Er: Thermodynamics of Pd-Er-H Systems

S. RAMAPRABHU and A. WEISS, *Ber. Bunsenges. Phys. Chem.*, 1989, **93**, (2), 146-148

The solubility of H in the intermetallic compounds Pd<sub>2</sub>Er<sub>5</sub>, Pd<sub>2</sub>Er<sub>3</sub>, PdEr, Pd<sub>4</sub>Er<sub>3</sub> and Pd<sub>3</sub>Er was measured by the pressure reduction method in the range  $1 < P/\text{mbar} < 1,000$  and  $473 < T/K < 1,148$ . The partial molar enthalpy of solution at infinite dilution ( $\Delta H_H^0$ ) was found to decrease with increase of Pd content. In Pd<sub>3</sub>Er, however, ( $\Delta H_H^0$ ) was anomalously high at  $-45.1$  kJ/mol, which indicates that the formation of the ordered structure results in an additional increase of exothermicity of H absorption reaction. The increase of exothermicity of H absorption in Pd<sub>3</sub>Er when compared to PdEr may be attributed to the smaller octahedral interstitial hole size. Pd<sub>2</sub>Er<sub>5</sub>, Pd<sub>2</sub>Er<sub>3</sub> and PdEr showed decomposition reactions by which Er hydride and the next intermetallic compound in the Pd-Er phase diagram with less Er content were formed.

## A Comparative Study of the Solubility and Thermodynamics of Hydrogen in Pd<sub>1-x</sub>RE<sub>x</sub> (RE=Dy, Gd, Sm, and Y; x=0.05 and 0.08) Solid Solution Alloys

S. RAMAPRABHU, N. RAJALAKSHMI and A. WEISS, *Ber. Bunsenges. Phys. Chem.*, 1989, **93**, (6), 686-696

Pressure-composition-temperature absorption isotherms have been determined for the Pd<sub>1-x</sub>RE<sub>x</sub> solid solution face centred cubic alloys in the pressure and temperature ranges of  $2 < P(H_2)/\text{mbar} < 1,000$  and  $473 < T/K < 873$  using the manometric method. The partial molar enthalpy of solution of H at infinite dilution ( $\Delta H_H^0$ ) becomes more exothermic with increasing  $x_{RE}$  due to the lattice expansion and an attractive metal-H interaction. The partial molar excess entropy of H solution at infinite dilution ( $\Delta S_H^{E,0}$ ) decreases with  $x_{RE}$ . The dependence of  $\Delta H_H^0$  of the "expanded" and "contracted" Pd<sub>1-x</sub>M<sub>x</sub> alloys on the size of the octahedral interstitial hole sites occupied by H atoms is discussed.

## The Thermophysical and Thermochemical Properties of RuO<sub>2</sub> from 0 to 1000K

E. H. P. CORDFUNKE, R. J. M. KONINGS, E. F. WESTRUM and R. SHAVIV, *J. Phys. Chem. Solids*, 1989, **50**, (4), 429-434

The heat capacity from 5 to 350K of RuO<sub>2</sub> has been measured by adiabatic calorimetry. For the thermochemical properties at room temperature  $C_p(298.15\text{K}) = (56.42 \pm 0.08) \text{Jmol}^{-1} \text{K}^{-1}$  and  $S^\circ(298.15\text{K}) = (46.15 \pm 0.05) \text{Jmol}^{-1} \text{K}^{-1}$  have been derived. Enthalpy increments relative to 298.15K have been measured by drop calorimetry from 410 to 757K. The thermodynamic functions, including the formation properties  $\Delta_f H^\circ(T)$  and  $\Delta_f G^\circ(T)$ , have been derived for temperatures up to 1,000K. Accurate thermodynamic data for RuO<sub>2</sub> is needed to model chemical processes occurring in nuclear accidents.

## CHEMICAL COMPOUNDS

### A New Tetradentate (N-)<sub>2</sub>S<sub>2</sub> Macrocyclic Ligand which is Highly Selective for Platinum(II) and Palladium(II)

E. KIMURA, Y. KUROGI, S. WADA and M. SHIONOYA, *J. Chem. Soc., Chem. Commun.*, 1989, (12), 781-783

A newly designed tetradentate macrocyclic ligand 10,10-dimethyl-9,11-dioxo-1,5-dithia-8,12-diazacyclotetradecane (H<sub>2</sub>L) in which two amide and two sulphide units act co-operatively showed high selectivity and efficiency for complex formation with Pt(II) and Pd(II) over Cu(II), Ni(II) and Co(II). Complexation of the ligand in MeOH-H<sub>2</sub>O (1:1) solution containing 2 equiv. of K<sub>2</sub>CO<sub>3</sub> (pH ~9) occurred quickly (~1 h) with Pd(OAc)<sub>2</sub> and slowly (~1 day) with K<sub>2</sub>PtCl<sub>6</sub> with simultaneous deprotonation of the amides to give the products [M<sup>II</sup>L]<sup>0</sup> isolated as yellow (100% yield) and colourless needles (~90% yield), respectively. The most remarkable feature of this ligand is that it does not form complexes with Cu(II), Ni(II) or Co(II) under the same conditions. This clear-cut recognition of Pt(II) and Pd(II) against other metal ions has no precedent.

### Scanning Tunnelling Microscopy of Rh<sub>4</sub> and Pt<sub>12</sub> Carbonyl Clusters Adsorbed on Graphite

T. FUJIMOTO, A. FUKUOKA, J. NAKAMURA and M. ICHIKAWA, *J. Chem. Soc., Chem. Commun.*, 1989, (13), 845-848

The images of the metal carbonyl clusters Rh<sub>4</sub>(CO)<sub>12</sub> and [NEt<sub>4</sub>]<sub>2</sub>[Pt<sub>12</sub>(CO)<sub>24</sub>] adsorbed on highly oriented pyrolytic graphite (HOPG) have been observed in well-ordered structures by scanning tunnelling microscopy. The humps observed in the line-scanning image of [NEt<sub>4</sub>]<sub>2</sub>[Pt<sub>12</sub>(CO)<sub>24</sub>] were determined to originate from a [Pt<sub>12</sub>(CO)<sub>24</sub>]<sup>2-</sup> cluster. Information on size and shape was obtained. Humps observed for Rh<sub>4</sub>(CO)<sub>12</sub> were in an ordered array and showed the arrangement of adsorbed Rh<sub>4</sub> clusters.

## ELECTROCHEMISTRY

### Anodic Oxidation of Propylene Carbonate on Platinum, Glassy Carbon and Polypyrrole. An "in-situ" FTIR Study

P. NOVÁK, P. A. CHRISTENSEN, T. IWASITA and W. VIELSTICH, *J. Electroanal. Chem. Interfacial Electrochem.*, 1989, **263**, (1), 37-48

The electrochemical oxidation of propylene carbonate (PC) was studied on Pt, glassy C and polypyrrole electrodes and production of CO<sub>2</sub> and other oxidation products was monitored by using in-situ FTIR. At a polished Pt electrode held at +2.0V (vs. Li/Li<sup>+</sup>), PC was stable but above +2.1V oxidation of PC started and this oxidation greatly accelerated above +3.5V (vs. Li/Li<sup>+</sup>). Oxidation of PC was also observed on polypyrrole covered Pt electrodes and on bare glassy-C electrodes, but their decomposition rate was much lower. In Li cells, direct oxidation of PC at high-potential cathodes contributes to self-discharge.

### Incipient Hydrrous Oxides—The Missing Link in Noble Metal Electrocatalysis

L. D. BURKE, J. F. HEALY, K. J. O'DWYER and W. A. O'LEARY, *J. Electrochem. Soc.*, 1989, **136**, (4), 1015-1021

Charged hydrrous oxide species are formed as surface-bound species at adatom sites on Pt at potentials as low as 0.2V (RHE) in acid media and, with precautions taken to minimise deactivation problems, many reactive organic compounds commence oxidation in this region. Recent spectroscopic data support the view that Pt(IV) species are present on Pt/Ru alloys at low potentials. The species formed on pure Pt in acid above 0.2V is assumed to be Pt(OH)<sub>6</sub><sup>2-</sup>-based species; the OH ligands not only accelerate many oxidation processes but inhibit certain reduction processes at the interface.

### Oxidative Dimerisation of Methane on Silver-Palladium Alloy Electrode, Connected with a Solid Oxide Electrolyte

V. D. BELYAEV, V. A. SOBYANIN, V. A. ARZHANNIKOV and A. D. NEUMIN, *Dokl. Akad. Nauk SSSR*, 1989, **305**, (6), 1389-1392

Studies were performed of oxidative dimerisation of CH<sub>4</sub> on 20%Pd-Ag electrode in high temperature solid oxide electrolyte of 0.9ZrO<sub>2</sub>+0.1Y<sub>2</sub>O<sub>3</sub> at atmospheric pressure, at 840°C, in a stream containing 10%CH<sub>4</sub> at 1ml/s. In electrolytic regime, O<sub>2</sub> was introduced into the reaction zone by passing of the electrolytic current through the cell. Dependences of stationary formation rate of C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub>, degree of CH<sub>4</sub> conversion and selectivity of C<sub>2</sub>-hydrocarbon formation, on the amount of O<sub>2</sub>-stream or the ratio of O<sub>2</sub>:CH<sub>4</sub> stream rates during oxidation of CH<sub>4</sub> in the electrocatalytic and catalytic systems are described. The results showed that this type of electrocatalytic dimerisation of CH<sub>4</sub> on Pd-Ag alloys is more convenient than those performed in other catalytic systems. During C<sub>2</sub>-hydrocarbons formation an important part is played by various electrolytic stages.

## Organic/Inorganic Electrodes (ORINELs) with Continuous Phase Components

B. AURIAN-BLAJENI, S. C. HOLLECK and B. H. JACKMAN, *J. Appl. Electrochem.*, 1989, 19, (3), 331-335

A new class of composite materials for electrodes comprising hydrated Ir oxide and polyaniline is described. The ORINELs (organic-inorganic electrodes) were prepared by electropolymerisation of a monomer in the pores of a disordered matrix which was formed by electrodeposition. The characteristic feature of ORINELs is the connectivity of the components. These electrodes have improved response to electrical perturbations as the distance travelled by the counter ions is reduced. Composites were characterised by impedance spectroscopy and current pulse experiments. The rate characteristics of the ORINEL are different from those of the inorganic layer.

## PHOTOCONVERSION

### Charge Transfer Process at Illuminated Semiconductor/Electrolyte Junctions Modified by Electrodeposition of Microscopic Metal Grain

P. ALLONGUE, E. SOUTEYRAND and L. ALLEMAND, *J. Electrochem. Soc.*, 1989, 136, (4), 1027-1033

Studies have shown that n-GaAs photoanodes can be very well stabilised in aqueous electrolytes by electrodeposition of microscopic, optically transparent Pt grains of various morphologies. Film morphology was the key parameter to effectively protect the surface against both chemical etching and photocorrosion. The mechanism of stabilisation by Pt grains was also studied by considering the surface state distributions, determined by photocapacitance experiments, at both bare and modified interfaces. The photovoltaic properties of the modified electrode are better than those of a bare electrode or of a solid Schottky barrier.

### In Situ Formation of Ru(II) Dinitrogen Complex $[\text{Ru}^{\text{II}}(\text{H-EDTA})\text{N}_2]^-$ and Its Reduction to $\text{NH}_3$ by Visible Light Irradiation of Pt or Rh Loaded CdS Particulate System in the Presence of EDTA as a Sacrificial Electron Donor

M. M. TAQUI KHAN and N. NAGESWARA RAO, *J. Mol. Catal.*, 1989, 52, (2), L5-L10

In situ formation of  $[\text{Ru}^{\text{II}}(\text{H-EDTA})\text{N}_2]^-$ , where H-EDTA is protonated ethylenediaminetetraacetate, by visible light irradiation of  $\text{K}[\text{Ru}^{\text{III}}(\text{H-EDTA})\text{Cl}]\cdot 2\text{H}_2\text{O}$  in the presence of Pt (or Rh)/CdS, through which  $\text{N}_2$  is bubbled, is reported. The coordinated N in the Ru(II) complex was catalytically reduced to  $\text{NH}_3$ . For the Pt/CdS particulate system  $\text{NH}_3$  was formed at 0.044 mol  $\text{NH}_3$  (mol cat.) $^{-1}\text{h}^{-1}$ . For Rh/CdS the rate reached 0.032 mol  $\text{NH}_3$  (mol cat.) $^{-1}\text{h}^{-1}$ . In the presence of a sacrificial electron donor, EDTA, the rate increased to 0.076 mol  $\text{NH}_3$  (mol cat.) $^{-1}\text{h}^{-1}$  for the Pt/CdS system.

## APPARATUS AND TECHNIQUE

### The Measurement of Instantaneous Local Heat Transfer Coefficients in a Circulating Fluidized Bed

R. L. WU, C. J. LIM and J. R. GRACE, *Can. J. Chem. Eng.*, 1989, 67, (2), 301-307

A small Pt instantaneous heat transfer probe has been developed and used to measure local instantaneous and time-averaged bed-to-wall heat transfer in a cold model circulating fluidised bed riser at three different heights for sand at a superficial gas velocity of 7m/s and for solids circulation fluxes up to  $\sim 70\text{kg/m}^2\text{s}$ . The probe consisted of a thin Pt film deposited on 1cm<sup>2</sup> glass protected by a thin plastic film. This probe design employs simple digital control to maintain the probe temperature constant, and the instantaneous heat flux from the probe and its temperature were determined relatively easily and accurately.

### Analytical Utility of Cylindrical Microelectrodes

S. T. SINGLETON, J. J. O'DEA and J. OSTERYOUNG, *Anal. Chem.*, 1989, 61, (11), 1211-1215

The behaviour and utility of 25 $\mu\text{m}$  diameter, 0.5-1.0 cm long Pt microelectrodes sealed in microcapillary pipettes has been studied for the cylindrical geometry. Chronoamperometry and cyclic staircase and square-wave voltammetry were performed on the ferri-ferrocyanide couple reversible system, and the observed behaviour was as predicted by theory. Plating and stripping of Ag illustrate the practicality of this electrode.

### Electrochemical Determination of Cholinesterase Activity and Indication of Its Inhibitors Using a Thick-Film Metallized Platinum Electrode

R. GRUSS, F. SCHELLER, M. J. SHAO and C. C. LIU, *Anal. Lett.*, 1989, 22, (5), 1159-1169

A thick film metallised Pt electrode operated in the voltammetric mode has been used to determine the cholinesterase activity in human serum and erythrocytes, which indicates the level of organophosphate intoxication caused by pesticides. Inhibitors of the enzyme can also be quantified by the electrode with cholinesterase either immobilised on the electrode or dissolved in the test medium.

### Solid Polymer Electrolyte-Based Electrochemical Oxygen Sensor

H.-Q. YAN and J.-T. LU, *Sens. Actuators*, 1989, 19, (1), 33-40

A new type of solid polymer electrolyte-based solid-state electrochemical  $\text{O}_2$  sensor with a working electrode consisting of a hydrophobic Teflon-bonded Pt black layer pressed on a piece of Nafion membrane, with a diffusion-controlling capillary in front, has been developed. The sensor showed fast response (95% response time of 1-2s), small temperature coefficient (0.3%/°C), and long-term stability.

### Planar Amperometric Enzyme-Based Glucose Microelectrode

M. KOUDELKA, S. GERNET and N. F. DE ROOIJ, *Sens. Actuators*, 1989, **18**, (2), 157-165

The fabrication and performance of a small (0.8mm x 3mm) amperometric glucose sensor containing a transducer consisting of a planar 3-electrode cell with Pt working and counter electrodes and Ag/AgCl reference, coupled with an immobilised glucose oxidase membrane, are described. An outer polyurethane membrane renders the sensor response less dependent on dissolved O concentration. The potential for development of a cheap, disposable glucose electrode for biomedical applications is shown by the easy, reproducible fabrication of the device, its linear response up to 40mM glucose with sensitivity of  $1.8 \pm 0.2 \text{ nA/mM}$ .

### Sensing Characteristics and Working Mechanism of Four-Probe Type Solid-State Hydrogen Sensor Using Proton Conductor

N. MIURA, T. HARADA and N. YAMAZOE, *J. Electrochem. Soc.*, 1989, **136**, (4), 1215-1219

A solid-state proton conductor (antimonic acid, AA) H<sub>2</sub> sensor composed of a basic electrochemical cell: sample gas, Pt<sub>1</sub>|AA sheet, Ag<sub>1</sub>, AA disc, Ag<sub>2</sub>, AA sheet|Pt<sub>2</sub>, AA sheet, sample gas, has been developed. With the two outer Pt electrodes short-circuited the potential difference between the two inner Ag probes was used as a signal output in this four-probe type sensor. Output was proportional to H<sub>2</sub> concentration (up to 1.3%) in air, and independent of relative humidity (7-90%).

### Effect of Platinum Distribution on the Hydrogen Gas Sensor Properties in Tin Oxide Thin Films

T. SUZUKI, T. YAMAZAKI, K. TAKAHASHI and T. YOKOI, *J. Mater. Sci.*, 1989, **24**, (6), 2127-2131

Tin oxide and Pt layers were deposited on oxidised Si wafers by ion-beam sputtering. Studies at 300°C of the H<sub>2</sub> sensing properties of undoped films and Pt-doped films showed that surface Pt, when annealed with the SnO<sub>2</sub> film at 500°C, increased the sensitivity and reduced the response time compared to those of undoped films. Longer annealing times tended to increase the optimum sensor thickness.

### Graphite Furnace Determination of Molybdenum by Palladium-Hydroxylamine Hydrochloride Matrix Modification

E. W. LOYA, *At. Spectrosc.*, 1989, **10**, (2), 61-65

The addition of an equal volume of a solution containing 0.1% Pd and 1.0% hydroxylamine hydrochloride greatly improved the accuracy of results obtained for the determination of Mo in natural waters by graphite furnace atomic absorption spectroscopy. Precision was improved by 47% and sensitivity by 36% by the reduced Pd matrix modifier.

### Use of Palladium(II) Chloride as a Colour-Forming Reagent for the Determination of N-Acetyl-L-Cysteine in Water and Fluimukan Injections

T. S. JOVANOVIĆ and B. S. STANKOVIĆ, *Anal.*, 1989, **114**, 401-403

Study of the formation of a complex between PdCl<sub>2</sub> and N-acetyl-L-cysteine (NAC: a biologically active substance used as an antidote for acetaminophen poisoning) in Britton-Robinson buffer solution at pH = 2.08-8.00 has led to the development of a simple, rapid and accurate spectrophotometric method for the determination of NAC in water and in Fluimukan injections in concentrations of 4.0-65.3µg/ml. The detection limit was 1.63µg/ml of NAC. The relative standard deviation varied from 0.63 to 1.92% for NAC in 8.16-32.64µg/ml.

### The Ammonia Sensitivity of Pd-Ir Alloy-Gate MOS Field-Effect Transistor

Z. WEIXIN and Z. LINGJUAN, *Sens. Actuators*, 1989, **19**, (2), 177-181

A new NH<sub>3</sub>-sensitive metal-oxide-semiconductor field-effect transistor (MOSFET) based on the use of a sputtered Pd-Ir alloy gate has been developed. Comparisons of sensitivity and selectivity of the Pd-Ir gate MOSFETs with data reported for others shows that these devices are highly sensitive and have good selectivity for NH<sub>3</sub>.

### Plasma-Edge Diagnostics Based on Pd-MOS Diodes

R. BASTASZ, B. L. CAIN, T. E. CAYTON, R. C. HUGHES and D. N. RUZIC, *J. Nucl. Mater.*, 1989, **162-164**, 587-592

Palladium metal-oxide-semiconductor (MOS) devices showed rapid, sensitive, dosimetric and reproducible response to energetic H<sub>2</sub>. Pd-MOS diodes can be regenerated when saturated with H by heating to 100-200°C for a few minutes. These properties, along with the devices small size, make it useful for plasma-edge diagnosis of H particle fluence when the energy distribution of the incident H is known. Pd-MOS diode sensors were used in the laboratory and in the ZT-40M reversed-field pinch to measure energetic H fluxes.

### Mechanism of Hydrogen Gas-Sensing at Low Temperatures Using Rh/TiO<sub>2</sub> Systems

G. MUNUERA, A. R. GONZÁLEZ-ELIPE, A. MUÑOZ, A. FERNÁNDEZ, J. SORIA, J. CONESA and J. SANZ, *Sens. Actuators*, 1989, **18**, (3 & 4), 337-348

The effects of H<sub>2</sub> adsorption on the conductivity of pressed pellets of a Rh/TiO<sub>2</sub> polycrystalline material were studied as a function of the degree of hydroxylation and reduction of the TiO<sub>2</sub> support. The results which were obtained by EPR, NMR and i.r. spectroscopic studies showed that this material can be an efficient sensor for H<sub>2</sub> at 295K in ambient atmosphere. A behaviour mechanism is proposed.

## HETEROGENEOUS CATALYSIS

### Evolution during Thermal Treatment of Pure and Lanthanum-Doped Pt/Al<sub>2</sub>O<sub>3</sub> and Pt-Rh/Al<sub>2</sub>O<sub>3</sub> Automotive Exhaust Catalysts. Transmission Electron Microscopy Studies on Model Samples

F. OUDET, A. VEJUX and P. COURTINE, *Appl. Catal.*, 1989, 50, (1), 79-86

Lanthanum-doped and undoped Pt/Al<sub>2</sub>O<sub>3</sub> and Pt-Rh/Al<sub>2</sub>O<sub>3</sub> automotive exhaust model catalysts were thermally aged step by step in air up to 900°C. Systematic transmission electron studies after each step of thermal ageing showed that the La exerted a stabilising effect on the Al<sub>2</sub>O<sub>3</sub> support and on the metallic dispersed phase. Results suggested that La does not modify the mechanism of thermal sintering but limits its extent at high temperature. With Rh-containing undoped samples, severe modifications were observed at low temperature.

### Enantioselective Hydrogenation of $\alpha$ -Keto Esters: Temperature-Programmed Reduction Study of Liquid-Phase Pt/Al<sub>2</sub>O<sub>3</sub> Hydrogenation Catalysts

H. U. BLASER, H. P. JALET, D. M. MONTI and J. T. WEHRLI, *Appl. Catal.*, 1989, 52, (1-2), 19-32

The effect of thermally pretreating Pt/Al<sub>2</sub>O<sub>3</sub> catalysts in H<sub>2</sub> on enantioselectivity and activity in the liquid-phase hydrogenation of  $\alpha$ -keto esters and the structure and oxidation state of the catalysts was studied by TPR, CO and N adsorption, and X-ray diffraction techniques. Thermal pretreatment in H<sub>2</sub> at 673K gave 15-20% higher optical yields of  $\alpha$ -hydroxy esters produced and the activity of the catalyst was up to three times higher for the activated catalysts. The TPR studies showed three well resolved peaks which were assigned to a Pt oxide shell on a Pt core at 200-400K, residual Pt salts at 400-550K and C deposits that originate from the liquid-phase preparation processes at 600-700K. The amount and reducibility of the Pt oxide was determined by TPR and correlated with the activity of the catalysts when strongly oxidised catalysts show lower activities.

### <sup>195</sup>Pt NMR Studies of Supported Catalysts

J. P. BUCHER, J. BUTTET, J. J. VAN DER KLINK, M. GRAETZEL, E. NEWSON and T. B. TRUONG, *Colloids Surf.*, 1989, 36, (2), 155-167

An overview of <sup>195</sup>Pt NMR data for Pt catalysts supported on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, and C carriers is presented. The fraction of atoms at the surface of the metal particles (the dispersion) can be derived from the spectra. Effects of surface treatment (oxidation-reduction, H absorption, strong metal-support interaction) are discussed in terms of the electronic local densities of states at the Fermi energy level. The qualitative features of the <sup>195</sup>Pt NMR spectrum are independent of the carrier material in the series SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, unless a high-temperature reduction is performed.

### Identification of Dispersed Platinum on $\gamma$ -Alumina by Laser-Raman Spectroscopy

K. OTTO, W. H. WEBER, G. W. GRAHAM and J. Z. SHYU, *Appl. Surf. Sci.*, 1989, 37, (2), 250-257

Laser-Raman spectroscopy has been used to identify highly dispersed Pt on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Under conditions favourable for dispersed Pt three peaks were observed at about 125, 335 and 590 cm<sup>-1</sup>. Results indicated that dispersed Pt coexists with particulate Pt even at concentrations as high as 30 wt.%Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The method can be used to study sintering and redispersion of Pt as a function of temperature and gas-phase.

### Aromatization of n-Hexane over Pt-KL Catalyst

I. MANNINGER, X. L. XU, P. TÉTÉNYI and Z. PAÁL, *Appl. Catal.*, 1989, 51, (1), L7-L11

Studies have shown that Pt on KL-zeolite promotes aromatisation, isomerisation and hydrogenolysis of n-hexane with a selective pattern similar to Pt/SiO<sub>2</sub> (EUROPT-1). Studies of the possible routes of aromatisation of n-hexane showed that olefins may be intermediates. The formation of cyclohexane in the aromatisation process at higher H<sub>2</sub> pressure has been confirmed by a <sup>14</sup>C radiotracer study.

### Study of Genesis of Active Phase of Platinum Catalysts for Complete Oxidation Modified by Rare Earths

V. A. DROZDOV, E. I. GRIGOROV, P. E. KOLOSOV, A. S. SEMIKOLENOV, A. L. CHUVILIN and P. G. TSYRUL'NIKOV, *Kinet. Katal.*, 1989, 30, (2), 422-428

Studies of the effect of rare earth cations on the character of thermolysis were made during thermodecomposition of H<sub>2</sub>PtCl<sub>6</sub>-Ln(NO<sub>3</sub>)<sub>3</sub> mixture in air (where Ln is La or Ce), and temperature at the end of the decomposition of the mixture, and phase state of the product were established. The decomposition of the mixture H<sub>2</sub>PtCl<sub>6</sub>-La(NO<sub>3</sub>)<sub>3</sub> proceeded with mutual acceleration of thermodecomposition of the components and was accompanied by formation of La oxychloride, with ionic Pt stabilised in its structure. The decomposition of the mixture H<sub>2</sub>PtCl<sub>6</sub>-Ce(NO<sub>3</sub>)<sub>3</sub> resulted in the formation of Ce(IV) oxide and metallic Pt.

### ESCA, SIMS, SEM and XRD Investigations of Pt-10%Rh Catalyst-Gauzes

A. P. V. ROSENSTIEL, W. H. J. BRUIS, G. H. VAN OS, P. R. MERTENS, O. A. KOEIMAN and K. H. BERRESHEIM, *Fresenius Z. Anal. Chem.*, 1989, 333, (4-5), 535-539

The nature and origin of harmful surface contaminants of spent Pt-10%Rh catalyst gauzes used in HNO<sub>3</sub> acid production has been determined by HR-SEM, ESCA, SIMS and XRD. All used gauzes showed a strong Rh surface enrichment (Rh:Pt ~ 2:1 at.%). The extent of Rh oxidation and the surface structure were determined for head, mid and tail gauze positions. Results showed that the degree of surface contamination could be greatly reduced and optimisation of several process parameters could improve the effective lifetime of the Pt-Rh catalyst.

### State of Palladium in Pd/Al<sub>2</sub>O<sub>3</sub> and Pd-Ce/Al<sub>2</sub>O<sub>3</sub> Catalysts from i.r.-Spectroscopic Data and Its Effect on Their Activity during CO Oxidation

A. L. TARASOV, V. A. SHVETS and V. B. KAZANSKII, *Kinet. Katal.*, 1989, 30, (2), 396-402

The i.r.-spectroscopy of adsorbed CO molecules and high temperature impulsive reoxidation studies were used to determine the effect of Pd and Ce interactions in deposited Pd-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts containing 0.5wt.% Pd and up to 2wt.% Ce, on their oxidative-reductive properties. The results showed that Pd promotes Ce reduction and Ce in return inhibits Pd reduction. Addition of Ce to the catalysts also results in a lower share of Pd surface available as crystallographic Pd(III) phase. Thus, under oxidation conditions, Pd/Al<sub>2</sub>O<sub>3</sub> and Pd-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts were more active during CO oxidation than during reduction.

### Temperature-Programmed Desorption Studies on Pd/CeO<sub>2</sub> after Methanol and Formic Acid Adsorption and Carbon Monoxide-Hydrogen Reaction

C. DIAGNE, H. IDRIS, I. PEPIN, J. P. HINDERMANN and A. KIENNEMANN, *Appl. Catal.*, 1989, 50, (1), 43-53

Temperature programmed desorption (TPD) studies on 3%Pd/CeO<sub>2</sub> (and 3%Pd/SiO<sub>2</sub>) catalysts after methanol and formic acid adsorption and CO-H<sub>2</sub> reaction suggested that formyl species are involved in CH<sub>3</sub>OH synthesis on Pd/CeO<sub>2</sub> catalysts, whereas on CeO<sub>2</sub> formate could be the main intermediate. After adsorption of formic acid on CeO<sub>2</sub> alone, CH<sub>3</sub>OH was desorbed with a maximum at 540-550K, indicating the possible hydrogenation of formate species to methanol. However, no CH<sub>3</sub>OH was observed after formic acid adsorption on 3%Pd/CeO<sub>2</sub>. Methanol desorption after CO-H<sub>2</sub> reaction on CeO<sub>2</sub> produced a TPD peak at 383K, possibly after methoxy hydrogenation, and a peak at 535K, possibly due to hydrogenation of formate. TPD after CO-H<sub>2</sub> reaction on 3%Pd/CeO<sub>2</sub> gave results similar to those after CH<sub>3</sub>OH adsorption.

### Effects of Palladium Particle Size and Palladium Silicide Formation on Fourier Transform Infrared Spectra of CO Adsorbed on Pd/SiO<sub>2</sub> Catalysts

L.-L. SHEU, Z. KARPINSKI and W. M. H. SACHTLER, *J. Phys. Chem.*, 1989, 93, (12), 4890-4894

The two major modes of CO adsorption on Pd/SiO<sub>2</sub>, bridging (B) and linear (L), reflect different extents of back-donation which is controlled, in part, by the local electron density at the adsorption site. The formation of B-CO increases with increasing Pd particle size, while that of L-CO decreases, indicating high electron density at Pd atoms in terraces of close-packed crystal faces. A B/L vs. metal dispersion curve was obtained for samples reduced at 300°C and 600°C. At 600°C significantly lower B/L values were obtained due to Pd silicide formation.

### Elementary Steps in the Formation of Highly Dispersed Palladium in NaY. I. Pd Ion Coordination and Migration

S. T. HOMEYER and W. M. H. SACHTLER, *J. Catal.*, 1989, 117, (1), 91-101

Detailed examination of the processes occurring during calcination of ion-exchanged Pd(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup>/NaY have shown that the ammine ligands are oxidised to N<sub>2</sub> and H<sub>2</sub>O in discrete steps yielding Pd(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> and Pd(NH<sub>3</sub>)<sub>2</sub><sup>2+</sup> in the zeolite supercages (calcination at <250°C), and Pd(NH<sub>3</sub>)<sub>2</sub><sup>2+</sup> (300°C) and Pd<sup>2+</sup> (400°C) in sodalite cages. The relative abundance and location of these ions can be controlled by the calcination programme. The Pd particle size after reduction depends on the location and co-ordination of Pd ions after calcination. A general principle is given in which the relative rates of nucleation and growth determine the particle size in the kinetic regime. Accordingly, highest dispersion of Pd is achieved by retaining the Pd ions in the supercages and maximising the diammine:tetraammine ratio.

### Highly Selective Dimerization of Ethylene over Pd-Mg-X Zeolite and Determination of Its Active Sites by Infrared Spectroscopy

T. BABA, K. NAKANO, S. NISHIYAMA, S. TSURUYA and M. MASAI, *Appl. Catal.*, 1989, 52, (1-2), 81-91

Studies of the dimerisation of ethylene over X-type zeolite containing Pd<sup>2+</sup> and an alkaline earth metal cation Mg<sup>2+</sup> were performed in order to prevent the decrease in the catalytic activity of Pd-Ca-X. X-type Pd<sup>2+</sup> and Mg<sup>2+</sup> containing zeolite had a high catalytic activity and a high selectivity for the ethylene dimerisation at 305K when it was pretreated with O<sub>2</sub> at 600K and a constant catalytic activity of X-type zeolite exchanged with Pd<sup>2+</sup> was maintained by Mg<sup>2+</sup> introduction. The i.r. spectroscopic results showed that Pd<sup>2+</sup> is the catalytically active species and the primary product, 1-butene, is formed over Pd<sup>2+</sup> sites in the zeolite.

### Conversions of Carbon Monoxide on Membrane Catalysts Based on Palladium Alloys. II. Interaction of CO and H<sub>2</sub> on Palladium-Nickel Alloys Covered by Dispersed Layers of Nickel and Copper

O. S. GUR'YANOVA, YU. M. SEROV, S. G. GUL'YANOVA and V. M. GRYAZNOV, *Kinet. Katal.*, 1989, 30, (2), 471-474

Studies of CO hydrogenation on Pd-Ni alloys covered by layers of Ni or Cu were performed at atmospheric pressure and 563-663K. The results showed that in addition to the normal yields of methane, ethanol and ethylene formed from CO and H<sub>2</sub> on the Pd-Ni alloys, after covering alloys with Ni, propane, propylene and a number of butanes and butenes were formed. On Cu covered surfaces, however, only methane was formed. Various methods of H<sub>2</sub> introduction into the reaction zone and their effects on activity and selectivity of the catalysts were also studied.

## Dissociation and Oxidation of Carbon Monoxide over Rh/Al<sub>2</sub>O<sub>3</sub> Catalysts

B. K. CHO and C. J. STOCK, *J. Catal.*, 1989, 117, (1), 202-217

Transient isotopic pulse experiments using a packed-bed reactor have shown significant CO dissociation activity during CO oxidation over Rh/Al<sub>2</sub>O<sub>3</sub> catalysts. Oxidation of CO proceeds via dissociative oxidation by its own O as well as via direct oxidation by gas phase O<sub>2</sub> on well dispersed Rh/Al<sub>2</sub>O<sub>3</sub>. The rates of CO dissociation and CO oxidation were of the same order of magnitude; under steady state conditions at 300°C, CO dissociation rate was ~1/2 that of direct oxidation. CO oxidation performance of Rh/Al<sub>2</sub>O<sub>3</sub> was better at low temperatures, possibly due to high CO dissociation activity. NO in the feedstream affected product distribution. The importance of CO dissociation kinetics is discussed, with reference to the different activities between single-crystal Rh surfaces and well-dispersed Rh/Al<sub>2</sub>O<sub>3</sub>.

## Selective Hydrogenation of Esters to Alcohols with a Catalyst Prepared from Rh<sub>2</sub>O<sub>3</sub>, Sn(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>, and SiO<sub>2</sub>: Evidence for Site Isolation

A. EL MANSOUR, J. P. CANDY, J. P. BOURNONVILLE, O. A. FERRETTI and J. -M. BASSET, *Angew. Chem., Int. Ed. Engl.*, 1989, 28, (3), 347-349

The Rh-Sn/SiO<sub>2</sub> catalyst, which was formed by reaction of Sn(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub> with Rh<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>, was more active and selective than Rh/SiO<sub>2</sub> for the hydrogenation of ethyl acetate to ethanol. The result indicates the ability of Sn atoms to isolate Rh atoms from their neighbours, as shown by the absence of bridged CO ligands after chemisorption of CO on the Rh-Sn/SiO<sub>2</sub> catalyst and leads to an increase in selectivity in the hydrogenation of ethyl acetate. The amount of ethanol increased from 57.2 for Sn:Rh = 0:1 to 97.2% for Sn:Rh = 1.7:1. At the same time the conversion of ethyl acetate increased from 1.32 to 4.66%.

## Shape-Selective Hydrogenation of Olefins with a Rhodium-Zeolite Catalyst

T. JOH, I. YAMAGUCHI and S. TAKAHASHI, *Nippon Kagaku Kaishi*, 1989, (3), 487-492

The shape-selective hydrogenation of olefins over Rh/NaY catalysts was studied on catalysts prepared by drying and calcinating of a Rh ion-exchange zeolite, [Rh(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>/NaY (1.5wt.% Rh), followed by treatment with CO at 130°C giving a Rh carbonyl cluster zeolite which was further treated with H<sub>2</sub> at 120°C. A pale brownish grey powder of Rh/NaY catalyst thus produced catalysed hydrogenation of various olefins with rates depending on the size/shape of olefin molecules. Selectivity of the catalyst was evaluated on the basis of comparison with Rh/C in the competitive hydrogenation of two kinds of olefins in a single medium. The results obtained showed that the active Rh species were located inside the zeolite cavities. The Rh/NaY catalyst may be applicable to shape-selective hydrogenation owing to the molecular sieve nature of the zeolite support.

## Structural Characterisation of Zeolite-Entrapped Rh<sub>6</sub> and RhFe Bimetallic Clusters and Their Catalysis in CO Hydrogenation Reaction

A. FUKUOKA, L.-F. RAO and M. ICHIKAWA, *Nippon Kagaku Kaishi*, 1989, (3), 561-568

Studies of Rh<sub>6</sub> and bimetallic RhFe clusters synthesised within NaY zeolite supercages showed Rh<sub>6</sub>(CO)<sub>16</sub> entrapped in NaY with i.r. spectrum of terminal carbonyl bands at 2,096 (s), 2,046 (w), and 2,020 (w), and a broad band at 1,760 (m) cm<sup>-1</sup> due to the triply bridging CO interacting with Al<sup>3+</sup> or Na<sup>+</sup> located on the wall of the NaY supercage. Prechemisorbed S on the reduced Rh<sub>6</sub>/NaY selectively suppressed the bridging CO chemisorption. Rh K-edge EXAFS studies of Rh<sub>6</sub>(CO)<sub>16</sub>/NaY provided evidence for the stoichiometric formation of hexanuclear Rh carbonyls within NaY supercage. The use of Rh<sub>6</sub>(CO)<sub>16</sub>/NaY catalyst led to the selective formation of olefin-rich C<sub>2</sub>-C<sub>4</sub> hydrocarbons in CO hydrogenation while the bimetallic RhFe/NaY catalysts showed higher selectivity for C<sub>1</sub>-C<sub>2</sub> alcohols.

## Synthesis of 2-Arylethanols by the Reaction of Benzyl Halides with CO/H<sub>2</sub> Using a Cobalt-Rhodium Bimetallic Catalytic System

M. ISHINO and T. DEGUCHI, *J. Mol. Catal.*, 1989, 52, (2), L17-L19

A novel reaction catalysed by a Co-Rh bimetallic system, which gives 2-arylethanols from benzyl halides and CO/H<sub>2</sub>, is reported. The activities of Rh, Co-Rh and Co, catalysts were determined. Co-Rh gave 2-phenylethanol in good yield in a one-step hydroxymethylation mechanism of benzyl halide. Co gave 2-phenylacetaldehyde almost exclusively and Rh gave 2-phenylethanol as well as the aldehyde. The results suggest that Co and Rh, respectively, catalyse the formylation of the benzyl halide and the reduction of the aldehyde.

## A Controlled Atmosphere in Situ X-Ray Diffraction Study of the Activation and Performance of Ammonia Synthesis Catalysts Derived from CeRu<sub>2</sub>, CeCo<sub>2</sub>, and CeFe<sub>2</sub>

A. P. WALKER, T. RAYMENT and R. M. LAMBERT, *J. Catal.*, 1989, 117, (1), 102-120

Highly active NH<sub>3</sub> synthesis catalysts derived from CeRu<sub>2</sub>, CeCo<sub>2</sub> and CeFe<sub>2</sub> intermetallic alloy precursors have been studied at up to 50 bar and 550°C, with precursor activation in H<sub>2</sub>, N<sub>2</sub>/H<sub>2</sub> and CO/H<sub>2</sub>. Precursor activation in N<sub>2</sub>/H<sub>2</sub> produced active and thermally stable Ce hydride systems which showed NH<sub>3</sub> activity decreasing in the order CeH<sub>2+x</sub>/Ru > CeH<sub>2+x</sub>/Co > CeH<sub>2+x</sub>/Fe. CeO<sub>2</sub>/(Ru, Co, Fe) catalysts produced by activation in CO/H<sub>2</sub> had a much lower activity for NH<sub>3</sub> synthesis. The special activity of the hydride based catalysts could be due to intimate interaction between the support phase and the ultradispersed transition metal particles.

## HOMOGENEOUS CATALYSIS

### Water Soluble, Zero-Valent, Platinum-, Palladium-, and Nickel-P(CH<sub>2</sub>OH)<sub>3</sub> Complexes: Catalysts for the Addition of PH<sub>3</sub> to CH<sub>2</sub>O

K. N. HARRISON, P. A. T. HOYE, A. G. ORPEN, P. G. PRINGLE and M. B. SMITH, *J. Chem. Soc., Chem. Commun.*, 1989, (16), 1096-1097

Studies have shown that the air-stable phosphine P(CH<sub>2</sub>OH)<sub>3</sub> forms H<sub>2</sub>O-soluble complexes [M{P(CH<sub>2</sub>OH)<sub>3</sub>}]<sub>n</sub> where M is Pt, Pd or Ni, which are catalysts for the production of the ligand itself from PH<sub>3</sub> and CH<sub>2</sub>O. The Pt complex was readily protonated by H<sub>2</sub>O, and a reaction scheme is given. The crystal structure of the Pd complex is also described showing that Pd atom is sheathed by the 12 alcohol groups which presents a highly hydrophilic surface to an approaching solvent.

### Competitive Routes of Decay of Pt(II) and Pt(IV) Ethyl Complexes in Aqueous Iodide Solutions. Estimation of Contribution of $\beta$ -Elimination

S. A. MITCHENKO and V. V. ZANASHCHIKOV, *Kinet. Katal.*, 1989, 30, (2), 297-302

Studies in the system NaI(1.3-3.3M)-HClO<sub>4</sub>(0.1-2.5M)-H<sub>2</sub>O showed that Pt(II) (0.02-0.16M) catalysed hydrogenation of ethylene to ethane, and hydrohalogenation of ethylene to ethyl iodide, at 353K, upon which the latter product reacted with Pt(II), again yielding ethylene or directly being reduced to ethane. A reaction mechanism, which included the intermediate formation of Pt(II) and Pt(IV) ethyl complexes is given. The basic route of decay of ethyl Pt(IV)- $\beta$ -eliminated complexes was determined in which the rate was twice the rate of complimentary reduction of C<sub>2</sub>H<sub>5</sub>Pt(IV) to C<sub>2</sub>H<sub>5</sub>Pt(II) and reducible elimination yielding C<sub>2</sub>H<sub>5</sub>I, when [Pt(II)]=0.1M. Ethyl Pt(II) complexes, in contrast to C<sub>2</sub>H<sub>5</sub>Pt(IV), decay in two ways: protolysis forming ethane and reoxidation to C<sub>2</sub>H<sub>5</sub>Pt(IV).

### Stereoelectronic Requirements of a Pd(0)-Catalyzed Cyclization. A Synthesis of allo-Pumiliotoxin 339B

B. M. TROST and T. S. SCANLAN, *J. Am. Chem. Soc.*, 1989, 111, (13), 4988-4990

Studies of a synthesis of allo-pumiliotoxin 339B, one of the most complex indolizidines, have established the geometric boundary for endo-type Pd-catalysed cycloalkylations to be between 5 and 6, and suggests an astonishing similarity of a Pd cationic leaving group to a conventional leaving group. With respect to pumiliotoxin, Pd-catalysed alkylations of vinyl epoxides provides a facile entry into the basic indolizidine ring system, allows a concise convergent strategy, and controls the creation of the proper stereochemistry at C(11) by chirality transfer. The potential of this sequence as a general route to this intriguing alkaloid family is suggested.

### Hydrocarboxylation of Polybutadiene on Palladium Complex Catalysts

A. L. LAPIDUS, S. YA. GROBOVENKO, A. V. GORYACHEVSKAYA, E. L. BERMAN and A. D. KAGARLITSKII, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, (6), 1390-1392  
Carboxylated polybutadiene was prepared by catalytic carboxylation of CO in the presence of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> catalyst. The results showed the possibility of introduction in polybutadiene of up to 60% of carboxylic groups in the presence of the Pd catalyst with PPh<sub>3</sub>, addition at 90-170°C and CO pressure of 2.0-14.0MPa, due to the presence of double-bonds in the polymer.

### Excimer Laser-Induced Homogeneous Catalytic Reactions

H. MORIYAMA, A. YABE, H. ARAKAWA, T. SAKAKURA and M. TANAKA, *Shokubai*, 1989, 31, (2), 100-103

Homogeneous hydrogenation of olefins under mild conditions by RhH(CO)(PPh<sub>3</sub>)<sub>3</sub> was accelerated by XeCl excimer laser irradiation. Significantly enhanced dark reactions were observed after periods of laser irradiation, which generated highly active catalytic species. The apparent quantum yield was estimated to be >1. However, hydroformylation of ethylene was not accelerated by laser irradiation. It is suggested that photoexcitation processes are involved in the catalytic cycle besides photodissociation of the CO ligand, as in the photocatalysed C-H bond activation of hydrocarbons using RhCl(CO)(PMe<sub>3</sub>)<sub>2</sub> different wavelength dependences were observed.

### Phosphanorbornadienes as Ligands in the Transition Metal-Catalyzed Synthesis of Fine Chemicals

D. NEIBECKER and R. RÉAU, *Angew. Chem., Int. Ed. Engl.*, 1989, 28, (4), 500-501

Highly active and selective Rh hydroformylation catalyst prepared from [Rh(CO)<sub>2</sub>Cl]<sub>2</sub> and phosphanorbornadienes in situ, were successfully used for hydroformylation of 1-hexene, styrene and ethyl acrylate at 25-80°C. The catalysts are suitable for the synthesis of aldehydes from a large variety of olefins, especially functionalised olefins, under very mild conditions. The results are promising for the selective production of hydratropaldehyde.

### Selective Dimerisation of Vinylketones into 1,5-Diketones Catalysed by RhCl(PMe<sub>3</sub>)<sub>3</sub>

I. P. KOVALEV, YU. N. KOLMOGOROV, A. V. IGNATENKO, M. G. VINOGRADOV and G. I. NIKISHIN, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, (5), 1098-1103

Detailed studies of  $\alpha$ - $\beta$ -dimerisation of methylvinylketones catalysed by RhCl(PMe<sub>3</sub>)<sub>3</sub> were performed and the feasibility of the preparatory synthesis of a number of  $\alpha$ -methylene substituted 1,5-diketones from vinylketones of various structure was studied. A selective method of synthesis of  $\alpha$ -methylene substituted 1,5-diketones by dimerisation of vinylketones was established; aromatic vinylketone was dimerised easier than the aliphatic one.

### Catalytic Reduction of Carbon Dioxide to Methane and Other Species via Formamide Intermediation: Synthesis and Hydrogenation of HC(O)NH<sub>2</sub> in the Presence of [Ir(Cl)(CO)(Ph<sub>3</sub>P)<sub>2</sub>]

L. VASKA, S. SCHREINER, R. A. FELTY and J. Y. YU, *J. Mol. Catal.*, 1989, **52**, (2), L11-L16

Synthesis and hydrogenation of formamide, HC(O)NH<sub>2</sub>, in the presence of [Ir(Cl)(CO)(Ph<sub>3</sub>P)<sub>2</sub>] and NH<sub>3</sub> as cocatalyst is reported as a process for CH<sub>4</sub> formation from CO<sub>2</sub>. The Ir(I) complex catalysed the synthesis of formamide from CO<sub>2</sub> + H<sub>2</sub> + NH<sub>3</sub>. Then neat formamide was catalytically hydrogenated using the Ir(I) complex to give CH<sub>4</sub>, N-methylformamide and N,N-dimethylformamide, as well as the five products which were produced by a non-catalytic "blank" run (in the absence of the Ir(I) complex). These complex and unexpected results are discussed in detail.

### Highly Selective Synthesis of Aldonolactones from Protected Alditols by Ruthenium Complex-Catalyzed Dehydrogenation. A Method of Converting Aldopentoses to Their Stereoisomers

M. SABURI, Y. ISHII, N. KAJI, T. AOI, I. SASAKI, S. YOSHIKAWA and Y. UCHIDA, *Chem. Lett. Jpn.*, 1989, (4), 563-566

Highly selective H transfer reaction of substituted diols catalysed by RuH<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub> was used during conversion of aldopentoses into their stereoisomers via protected pentitols, and the selective transformations of L-arabinose and L-ribose to protected L-lyxonolactone and D-ribonolactone, respectively, were thus achieved. It is suggested that high selectivities will be achievable for the lactonisations of 2,3-disubstituted 1,4-diols when the difference in the steric bulkiness between the two substituents is sufficient.

## FUEL CELLS

### Dual Modification of Platinum Electrode by Bonding It to Solid Polymer Electrolyte (SPE) and by Its Alloy Formation as Methanol Fuel Cell Anode

A. ARAMATA, *Shokubai*, 1989, **31**, (2), 52-55

In the development of a highly active anode for a CH<sub>3</sub>OH fuel cell Pt metal was first bonded to SPE, then Pt-SPE was modified by other metals such as Ru, Sn and Mo. Pronounced activity toward CH<sub>3</sub>OH electro-oxidation was observed. The alloy formation with other metals further increased the activity of Pt-SPE. The highest activity was obtained for the ternary Pt-Ru-Sn alloy-SPE electrode with current density of 50 mA/cm<sup>2</sup> at 0.4 V vs. RHE at 60°C in 1M CH<sub>3</sub>OH + 0.5M H<sub>2</sub>SO<sub>4</sub>. Ternary alloy catalysts were more active than binary alloy catalysts. Activity was also affected by the presence of amorphous alloy phases. The proper choice of the second metals for ternary or quaternary Pt alloy is suggested.

### A Nafion®-Bound Platinized Carbon Electrode for Oxygen Reduction in Solid Polymer Electrolyte Cells

A. K. SHUKLA, P. STEVENS, A. HAMNETT and J. B. GOODENOUGH, *J. Appl. Electrochem.*, 1989, **19**, (3), 383-386

A full-factorial statistical method has been used to optimise the amount of binder, the compaction load and the compaction time in order to fabricate Nafion-bound C electrodes containing Pt and pyrolysed Co meso-tetramethoxyphenylporphyrin (CoTMPP). The electrodes are used for O reduction in solid polymer electrolyte fuel cells, and it has been found that incorporation of Nafion gel with the C substrate facilitates its binding with the Nafion membrane of such a fuel cell. The polarisation behaviour of a Nafion-bound C electrode containing Pt is compared to that containing CoTMPP.

### Electrochemical Control of the Partial Oxidation of Olefins with Fuel Cell Reaction System

K. OTSUKA, Y. SHIMIZU, I. YAMANAKA and T. KOMATSU, *Shokubai*, 1989, **31**, (2), 48-51

When a positive potential was applied to the (C<sub>3</sub>H<sub>6</sub>, H<sub>2</sub>O, Pd|H<sub>3</sub>PO<sub>4</sub>|Pt, O<sub>2</sub>) fuel cell system at 366K, the oxidation of propylene to the Wacker type product, acetone, was enhanced dominantly. The  $\pi$ -allyl oxidation products, acrolein and acrylic acid, were obtained when a negative potential was applied. Addition of H<sub>2</sub>, PdCl<sub>2</sub> and HCl to the electrolyte enhanced the rate of acetone formation remarkably. The selectivity to the two types of oxidation depended on the relative concentrations of Pd<sup>0</sup> (active sites of  $\pi$ -allyl oxidation) and Pd<sup>2+</sup> (active sites of Wacker oxidation) coexisting at the interface between Pd-electrode and H<sub>3</sub>PO<sub>4</sub> electrolyte.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Magneto-Optical Properties in Ultrathin Co/Pd and Co/Pt Multilayer Films

Y. OCHIAI, S. HASHIMOTO and K. ASO, *Jpn. J. Appl. Phys.*, 1989, **28**, (4), L659-L660

A polar Kerr loop tracer has been used to characterise the magnetic properties of Co/Pt and Co/Pd multilayer films prepared by magnetron-type sputtering. Both multilayer films had perpendicular magnetic anisotropy when the Co layer became < 10 Å. The Kerr rotation angle  $\theta_k$  was enhanced at the film thickness  $t < 500\text{Å}$  and the Kerr remanence: saturation ratio became  $\theta_{kr}:\theta_k = 1$  at  $t < 200\text{Å}$ . In the Co/Pd system, the coercive force was influenced by the sputtering gas pressure. Simultaneous enhancement in  $\theta_k$  and  $\theta_{kr}:\theta_k$  is assumed to originate from the optical and magneto-optical parameters and the perpendicular magnetic anisotropy, respectively. Ultrathin Co/Pd and Co/Pt multilayer films are suitable for magneto-optical media due to their strong corrosion resistance.

## Annealing Effect on Magnetic Characteristics of Pt/MnSb Multilayered Films

T. KAWANABE and M. NAOE, *J. Phys. (Paris)*, 1989, 49, (12), 1783-1784

Magnetic properties of PtMnSb multilayered films depend on the annealing temperature and time. Distinct perpendicular anisotropy has been found in the films composed of MnSb layers 50Å thick and Pt layers ~13Å thick after annealing at 400°C for 2.5h in vacuum. These films have perpendicular anisotropy constant  $K_u$  of  $4 \times 10^3$  erg/cc.

## Pt and PtSi<sub>x</sub> Schottky Contacts on n-Type β-SiC

N. A. PAPANICOLAOU, A. CHRISTOU and M. L. GIPE, *J. Appl. Phys.*, 1989, 65, (9), 3526-3530

The electrical and annealing characteristics of novel Schottky barrier rectifying contacts formed by e-beam-deposited Pt on n-type β-SiC have been studied. Short annealing cycles at 350-800°C led to the formation of a mixed structure of PtSi<sub>x</sub> and PtC at the Pt/SiC interface, as shown by migration of Pt into the SiC above 350°C. The barrier height was found to increase from 0.95 to 1.35eV with increasing annealing temperature. The rectifying characteristics improved following an initial 350°C anneal and remained relatively stable up to 800°C.

## A Novel Process for High-Performance Schottky Barrier PMOS

B.-Y. TSUI and M.-C. CHEN, *J. Electrochem. Soc.*, 1989, 136, (5), 1456-1459

A novel process for high performance rinsed asymmetric Schottky barrier PMOS transistors with a Schottky barrier junction source and a p-n junction drain is described. PtSi is used to form the source Schottky junction. Spacer oxide is not necessary for this process to isolate the poly-Si gate and the source PtSi; thus the source PtSi may directly contact the inverted channel. The new Schottky barrier PMOS can circumvent the drawbacks of conventional Schottky barrier PMOS.

## Pt/Ti/p-In<sub>0.53</sub>Ga<sub>0.47</sub>As Low-Resistance Nonalloyed Ohmic Contact Formed by Rapid Thermal Processing

A. KATZ, W. C. DAUTREMONT-SMITH, S. N. G. CHU, P. M. THOMAS, L. A. KOSZI, J. W. LEE, V. G. RIGGS, R. L. BROWN, S. G. NAPHOLTZ, J. L. ZILKO and A. LAHAV, *Appl. Phys. Lett.*, 1989, 54, (23), 2306-2308

Very low resistance nonalloyed ohmic contact of Pt/Ti to  $1.5 \times 10^{19}$  cm<sup>-3</sup> Zn-doped In<sub>0.53</sub>Ga<sub>0.47</sub>As were formed by e-beam evaporation of Pt/Ti films onto the ternary epitaxial layer and subsequently subjected to rapid thermal processing at temperatures over the region 300-600°C for 30s. These contacts were ohmic as deposited with a specific contact resistance value of  $3.0 \times 10^{-4}$  Ωcm<sup>2</sup>. A very limited interfacial reacted layer (20nm thick) was observed between the Ti and the InGaAs as a result of heating at 450°C for 30s.

## System Bi<sub>2-x</sub>Pb<sub>x</sub>Pt<sub>2-x</sub>Ru<sub>x</sub>O<sub>7-2x</sub>: A Pyrochlore Series with a Metal-Insulator Transition

G. MAYER-VON KÜRTHY, W. WISCHERT, R. KIEMEL, S. KEMMLER-SACK, R. GROSS and R. P. HUEBENER, *J. Solid State Chem.*, 1989, 79, (1), 34-45

The pyrochlore compounds Bi<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub> (insulator) and Pb<sub>2</sub>Ru<sub>2</sub>O<sub>6.5</sub> (metallic conductor) form a continuous series of solid solutions Bi<sub>2-x</sub>Pb<sub>x</sub>Pt<sub>2-x</sub>Ru<sub>x</sub>O<sub>7-2x</sub>. Increasing substitution of Pt by Ru resulted in a gradual insulator-metal transition. Metallic conductivity was found for a substitution level of  $x \geq 1.5$ .

## High-Barrier Height Metal-Insulator-Semiconductor Diodes on n-InP

Y. S. LEE and W. A. ANDERSON, *J. Appl. Phys.*, 1989, 65, (10), 4051-4056

Metal-insulator-semiconductor diodes have been made using Pd, Ni and Au contacts on n-InP covered by 40Å chemically grown oxide. Pd devices gave the highest barrier height of 0.8eV and the lowest reverse saturation current density. The oxide had a refractive index of 1.4-1.6 and a composition of mainly In<sub>2</sub>O<sub>3</sub> + some InPO<sub>3</sub> near the surface and mixed oxide + InP near the interface. The temperature dependence of the barrier height was determined.

## Anodically Electrodeposited Iridium Oxide Films (AEIROF) from Alkaline Solutions for Electrochromic Display Devices

K. YAMANAKA, *Jpn. J. Appl. Phys.*, 1989, 28, (4), 632-637

Anodically electrodeposited Ir oxide films from alkaline solutions have been studied for application to electrochromic devices. Micro-crystalline (diameter 15Å) films obtained by the electrolysis of aqueous alkaline solutions containing IrCl<sub>4</sub>, oxalic acid and K<sub>2</sub>CO<sub>3</sub> showed good electrochromic reversibility. The colouration efficiency of the films was about 1/3 that of typical evaporated W oxide films, and the response rate measured by the amount of injected charge was about double. The cycle lives of the cells, composed of electrodeposited Ir oxide films, 1M H<sub>3</sub>PO<sub>4</sub>-NaOH (pH=3-5), and an activated C cloth, were  $> 8 \times 10^6$  with a 0.6V, 1Hz continuous wave.

## MEDICAL USES

### Shape-Selective Targeting of DNA by (Phenanthrenequinone diimine) rhodium(III) Photocleaving Agents

A. M. PYLE, E. C. LONG and J. K. BARTON, *J. Am. Chem. Soc.*, 1989, 111, (12), 4520-4522

Phenanthrenequinone diimine (phi) complexes of Rh(III) are described as a family of new, highly efficient, photocleaving reagents which appear to recognise ostensibly B-form DNA sites on the basis of considerations of shape. Rh(phen)<sub>2</sub>phi<sup>3+</sup>, where phen is phenanthroline, is useful as a probe of local variations in major groove size. These complexes may find application both in vitro and in vivo.