

# ABSTRACTS

of current literature on the platinum metals and their alloys

## PROPERTIES

### Optical Properties of Coloured Platinum Intermetallic Compounds

J. HURLY and P. T. WEDEPOHL, *J. Mater. Sci.*, 1993, 28, (20), 5648–5653

The optical properties of PtAl<sub>2</sub> were changed by addition of 5–25 % Cu by mass. The colour of PtAl<sub>2</sub> changed from brass-yellow through orange to copper-pink. Adding Cu increased the lattice parameter of the simple fluorite structure PtAl<sub>2</sub> by ~ 0.8 %, but not its structure. Also the addition of Cu produces a progressive lowering of the reflectivity at the red end of the visible spectrum.

### Phase Equilibria in the Pt-In-P System

C. F. LIN, S. E. MOHNEY and Y. A. CHANG, *J. Appl. Phys.*, 1993, 74, (7), 4398–4402

Phase equilibria in the Pt-In-P system have been determined at 725 and 600°C by XRD and electron probe microanalysis. The observed binary phases were consistent with data in the literature; three ternary phases were found. A tie-line transition from InP–Pt<sub>3</sub>In<sub>7</sub> at low temperature to In–PtP<sub>2</sub> at high temperatures was found between 600 and 725°C from both bulk phase equilibria and PtIn<sub>7</sub>/InP thin film samples. Enthalpy of formation of PtP<sub>2</sub> at 298 K was ~ -350 ± 40 kJ/mol. From the phase equilibria, Pt<sub>3</sub>In<sub>7</sub> may be useful as a stable contact material to InP.

### Quasicrystalline (Al,Pd)-Phase in Dilute Al-Si-V-Pd Films for Use as Reliable Metallizations in Ultralarge Scale Integration

A. G. DIRKS and A. E. M. DE VEIRMAN, *Scr. Metall. Mater.*, 1993, 29, (8), 1017–1022

A study of the Al-Si-V-Pd alloy has been performed to assess its use in ULSI, and to examine its high resistance to electromigration, which occurs at a current density of 2.10<sup>6</sup> A/cm<sup>2</sup> at 180°C. In DC magnetron sputtered Al<sub>0.82</sub>Si<sub>0.10</sub>V<sub>0.1</sub>Pd<sub>0.1</sub> alloy films (Al, Pd) precipitates were observed upon annealing at 450°C, being located at the Al grain boundaries.

### Fe/Pd Nano-Multilayers Prepared by Vapour Deposition, and Their Magnetic Anomaly

F. PAN, T. YANG, J. ZHANG and B. X. LIU, *J. Phys.: Condens. Matter*, 1993, 40, (5), L507–L514

The magnetic properties of Fe/Pd nano-multilayers prepared by electron beam vapour deposition are reported. The magnetic moment per Fe atom in the multilayers was greatly enhanced when the Fe layer thickness was < 6.5 nm: up to 3.27 μ<sub>B</sub> at an Fe layer thickness of 1.6 nm, and there was an increased tendency towards perpendicular magnetisation as the thickness of the Fe layer decreased. The enhancement may be due to the formation of a Fe-enriched phase with f.c.c. structure, at the Fe/Pd interfaces.

### The Reflectance of Solid-Phase Epitaxial Pd/Ge Film on GaAs and Its Application for VCSELs Array

W.-X. CHEN, P.-F. JIAO, J.-H. ZHAO, S.-M. WANG, S.-C. GUAN and Q.-X. CHEN, *Solid State Commun.*, 1993, 88, (6), 461–463

A novel technique for producing vertical cavity surface-emitting lasers (VCSELs) arrays is described, which uses solid-phase epitaxial Pd/Ge thin films as ohmic contacts to GaAs. The Pd/Ge ohmic contact to GaAs had a resistivity of 5 × 10<sup>-7</sup>/cm<sup>2</sup> on 10<sup>16</sup>/cm<sup>3</sup> n-GaAs. The reflectivity of the non-alloyed Pd/Ge film on GaAs is suitable for use as both the reflectors and electrodes in the laser array.

### Structural Analysis of Polymer-Protected Palladium/Rhodium Bimetallic Clusters Using EXAFS Spectroscopy

M. HARADA, K. ASAKURA, Y. UEKI and N. TOSHIMA, *J. Phys. Chem.*, 1993, 97, (41), 10742–10749

Structures of colloidal dispersions of Pd/Rh bimetallic clusters prepared by refluxing solutions of their salts in H<sub>2</sub>O/EtOH in the presence of poly-(N-vinyl-2-pyrrolidone) were investigated by EXAFS. The Pd-Rh bond distance, ~ 2.7 Å in the alloy foil, is equal to that of Pd-Pd and Rh-Rh in Pd and Rh foils, respectively. Peak height differences between the Pd foil and the Pd/Rh(1/1) alloy foil and between Rh foil and the same alloy foil show that the disorders are all about the same, even at room temperature.

### Electrical Resistance and Thermoelectric Power of Ordered Fe<sub>25</sub>Pd<sub>75-x</sub>Au<sub>x</sub> Alloys

N. I. KOUROV, L. N. TYULENEV and YU. A. VERESHCHAGIN, *Fiz. Metal. Metallov.*, 1993, 75, (6), 75–79

The electrical resistance and thermoelectric power of ordered Fe<sub>25</sub>Pd<sub>75-x</sub>Au<sub>x</sub> alloys, where x ≤ 37.5 at. %, were studied at intervals between 4.2–1300 K. The dependencies of the temperature and concentration characteristics were established during the phase transfer from ferromagnetic (x < 7.5 at.%) to antiferromagnetic (x > 15 at.%) alloys, and also on the boundary of stability of the modified phases (x ≥ 25 at.%).

### The Specific Volumes of Pd<sub>40</sub>Ni<sub>10</sub>P<sub>20</sub> in the Liquid, Glass, and Crystallized States

K. C. CHOW, S. WONG and H. W. KUI, *J. Appl. Phys.*, 1993, 74, (9), 5410–5414

The specific volumes of Pd<sub>40</sub>Ni<sub>10</sub>P<sub>20</sub> in the liquid (827–1196 K), glass (300–593 K), and crystallised state (300–593 K) are reported. Purity was very important for the molten state measurements. The intersection points of the specific volume curves of the liquid (both stable and metastable), glass and crystallised state are 573 ± 80 and 492 ± 80 K (extrapolated values), respectively. The specific volume of the relaxed glass is 0.25% above that of the crystallised state.

### The Shape Memory Effect in a Ti<sub>50</sub>Pd<sub>50</sub> Alloy

K. OTSUKA, K. ODA, Y. UENO, M. PIAO, T. UEKI and H. HORIKAWA, *Scr. Metall. Mater.*, 1993, **29**, (10), 1355–1358

High temperature tensile tests for the Ti<sub>50</sub>Pd<sub>50</sub> alloy, which exhibits the highest transformation temperatures are reported using a button of the alloy made by plasma melting. To improve the shape memory characteristics the critical stress for slip has to be increased by adding a ternary element, and the parent phase has to be strengthened by age hardening, and by a heat-mechanical treatment. Adding Ni to the Ti-Pd alloy system improved the shape memory characteristics.

### Magnetic Order in Pd<sub>2</sub>TiIn: A New Itinerant Antiferromagnet?

K. U. NEUMANN, J. CRANGLE, R. K. KREMER, N. K. ZAYER and K. R. A. ZIEBECK, *J. Magn. & Magn. Mater.*, 1993, **127**, (1–2), 47–51

The bulk magnetic properties of the intermetallic compound Pd<sub>2</sub>TiIn which has the Heusler L<sub>2</sub> structure are reported. The material orders antiferromagnetically at  $c \sim 110$  K. The effective paramagnetic moment obtained from the Curie-Weiss behaviour of the susceptibility is  $4.9 \mu_B$ , which is much higher than can be expected from a localised moment associated with the Ti atoms. This suggests that the material is probably an itinerant antiferromagnet with finite-temperature properties characterised by spin fluctuations.

### Characterization of Mechanical Properties in the Ir-Nb-Zr Intermetallic System

A. M. GYURKO and J. M. SANCHEZ, *Mater. Sci. Eng.*, 1993, **A170**, (1–2), 169–175

The mechanical properties of very high melting intermetallic compounds in the Ir-Nb-Zr system are examined. Two related high temperature L<sub>1</sub><sub>2</sub> intermetallic compounds Ir<sub>3</sub>Nb (1) and Ir<sub>3</sub>Zr (2) have similar lattice parameters, and melting points of 2450 and 2280°C, respectively. (1) has twice the strength of (2). A ternary compound Ir<sub>0.71</sub>Nb<sub>0.21</sub>Zr<sub>0.08</sub> has a high temperature strength greater than that of either (1) or (2). Total energy electronic structure calculations confirmed the similarity in the cohesive properties of the binary compounds and suggest that differences in the density of states at the Fermi level may explain their dissimilar mechanical behaviour.

### The Magnetic Properties of Iridium in Mixed-Metal Oxides

A. V. POWELL, J. G. GORE and P. D. BATTLE, *J. Alloys Compd.*, 1993, **201**, 73–84

The magnetic susceptibilities of Ir mixed metal oxides have been measured as functions of temperature and applied magnetic field. Oxides Sr<sub>3</sub>IrO<sub>6</sub>, BaLaNiIrO<sub>6</sub> and BaLaCoIrO<sub>6</sub> order antiferromagnetically at 12, 87 and 56 K, respectively. BaLaFeIrO<sub>6</sub> has a spin-glass transition at 65 K. La<sub>2</sub>NiIrO<sub>6</sub> and La<sub>2</sub>CuIrO<sub>6</sub> order as weak ferromagnets at 80 and 70 K, respectively. La<sub>2</sub>Mg<sub>1-x</sub>Zn<sub>x</sub>IrO<sub>6</sub> changes from antiferromagnetism, with  $T_N = 11.7$  K, when  $x = 0$ , to ferromagnetism with  $T_c = 9.5$  K and  $\mu_{\text{eff}} = 0.4 \mu_B$ , when  $x = 1$ .

### Phase Diagram and Electrical Behavior of Silicon-Rich Iridium Silicide Compounds

C. E. ALLEVATO and C. B. VINING, *J. Alloys Compd.*, 1993, **200**, 99–105

The Ir-Si phase diagram on the Si-rich side has been investigated by XRD, DTA, metallography and other techniques. An attempt to prepare eight Si-rich compounds was made; however, only IrSi, Ir<sub>2</sub>Si<sub>3</sub>, Ir<sub>3</sub>Si<sub>4</sub>, Ir<sub>3</sub>Si<sub>5</sub>, and IrSi<sub>3</sub> were identified. Ir<sub>2</sub>Si<sub>3</sub>, Ir<sub>3</sub>Si<sub>4</sub>, and IrSi<sub>3</sub> were not found. IrSi<sub>3</sub> was polymorphic with orthorhombic and monoclinic unit cells in the high and low temperature forms. IrSi and IrSi<sub>3</sub> exhibit nearly temperature-independent electrical resistivities of  $(5-10) \times 10^{-6}$  ohm m. Ir<sub>2</sub>Si<sub>3</sub> and Ir<sub>3</sub>Si<sub>4</sub> have metallic behaviour, and Ir<sub>3</sub>Si<sub>5</sub> is semiconducting. A eutectic alloy with  $80 \pm 1$  at. % Si was observed between IrSi<sub>3</sub> and Si.

## ELECTROCHEMISTRY

### A Study of Cathodic Oxygen Reduction at Platinum Using Microelectrodes

D. PLETCHER and S. SOTIROPOULOS, *J. Electroanal. Chem.*, 1993, **356**, (1 and 2), 109–119

Cathodic reduction of O<sub>2</sub> was studied at a Pt rotating disc electrode and Pt microelectrodes in neutral and basic aqueous solutions. The limiting current densities for the reduction waves at the Pt electrodes are explained by the fact that the apparent number of electrons involved in the reduction is a strong function of the mass-transfer coefficient,  $k_m$ , and the reduction changes from a 4-electron to a 2-electron process with increasing rate of mass transport. H<sub>2</sub>O<sub>2</sub> is the major product where there is a large  $k_m$ .

### Ellipsometry of Hydrated Platinum Oxide Layers and Electrodispersed Platinum Surfaces Resulting from Their Electroreduction

J. O. ZERBINO, C. PERDRIEL and A. J. ARVIA, *Thin Solid Films*, 1993, **232**, (1), 63–67

The ellipsometric characteristics of relatively thick (400–700 nm) hydrated Pt oxide layers (HPtOLs) produced by oxidation-reduction cycling at 0–2.4 V in 1 M H<sub>2</sub>SO<sub>4</sub> were studied, together with the surface topography of electrodispersed Pt electrodes (EDPtEs) obtained by electroreducing the HPtOLs, at 25°C. The H<sub>2</sub>O content of HPtOLs increases with increasing layer thickness. The EDPtE has a rough structure with a metal : void ratio of  $\sim 0.5$ .

### Preparation and Characterization of a Composite Palladium-Ceramic Membrane

J. P. COLLINS and J. D. WAY, *Ind. Eng. Chem. Res.*, 1993, **32**, (12), 3006–3013

Composite Pd-ceramic membranes with Pd films of 11.4–20  $\mu\text{m}$  were made by depositing Pd film inside asymmetric tubular ceramic membranes by electroless plating. The membranes had both high H<sub>2</sub> permeability and selectivity. The H<sub>2</sub>/N<sub>2</sub> selectivity for a membrane with a 11.4  $\mu\text{m}$  Pd film was 380 at 823 K at a transmembrane pressure difference of 1500 kPa.

## Electrochemical and Corrosion Behaviour of Intermetallide Systems of Ti<sub>2</sub>Pd and TiPd and Ti with Electrodispersed Palladium Layers

L. P. KORNIENKO, N. D. TOMASHOV and G. P. CHERNOVA, *Zashch. Met.*, 1993, 29, (3), 359–367

Studies of the dissolution rates of Ti and Pd electrodes, and also of Ti and Pd from intermetallides Ti<sub>2</sub>Pd and TiPd, in anodic and cathodic regions were performed under corrosion potentials in 10 % H<sub>2</sub>SO<sub>4</sub> at 100°C. Intermetallides Ti<sub>2</sub>Pd and TiPd formed on the Ti surface during the electrodispersion of Pd alloys, followed by annealing, appeared to be an effective cathode, giving corrosion protection to the system.

## Capability of Permeate Hydrogen through Palladium-Based Membranes for Acetylene Hydrogenation

N. ITOH, W.-C. XU and A. M. SATHE, *Ind. Eng. Chem. Res.*, 1993, 32, (11), 2614–2619

Hydrogen permeation through pure Pd, Pd<sub>93</sub>Ni<sub>7</sub>, Pd<sub>93</sub>Ru<sub>7</sub> and Pd<sub>77</sub>Ag<sub>23</sub> membranes was used to hydrogenate C<sub>2</sub>H<sub>2</sub> at 373 K and atmospheric pressure. H<sub>2</sub> was supplied by a permeation mode through the membrane and a premixed mode. For higher C<sub>2</sub>H<sub>4</sub> conversions the order in the membranes was Pd > Pd<sub>93</sub>Ni<sub>7</sub> > Pd<sub>77</sub>Ag<sub>23</sub> > Pd<sub>93</sub>Ru<sub>7</sub>. The H<sub>2</sub> which permeated through the Pd-based membrane is more active than H<sub>2</sub> from the premixed mode.

## PHOTOCONVERSION

### A New Linkage Isomer of RhCl<sub>3</sub>(DMSO)<sub>3</sub>: Photochemical Synthesis, Crystal Structure, and Reactivity of *mer,trans*-RhCl<sub>3</sub>(DMSO)<sub>2</sub>(DMSO)

E. ALESSIO, P. FALESCHINI, A. S. SANTI, G. MESTRONI and M. CALLIGARIS, *Inorg. Chem.*, 1993, 32, (25), 5756–5761

The photochemical isomerisation of the title compound (1) to the new linkage isomer *mer,trans*-RhCl<sub>3</sub>(DMSO)<sub>2</sub>(DMSO) (2) was performed in order to study the effect of light on the equilibria between the neutral Rh-DMSO isomers. Complex (2) is thermodynamically unstable compared to (1). The two isomers react stereospecifically with N ligands by following different paths and produce isomeric products.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Iridium Coatings on Carbon-Carbon Composites Produced by Two Different Sputtering Methods: A Comparative Study

K. MUMTAZ, J. ECHIGOYA, T. HIRAI and Y. SHINDO, *J. Mater. Sci. Lett.*, 1993, 12, (18), 1411–1412

High modulus C fibres were used to make C-C composite substrates. Ir was r.f. and DC sputtered onto one side of the composite. DC sputtering produced interconnected islands and some uncovered substrate. The r.f. sputtered coatings were extremely fine and uniform before and after high-temperature heat treatment.

## Low-Temperature Chemical Vapor Deposition of Ruthenium Dioxide from Ruthenium Tetroxide: A Simple Approach to High-Purity RuO<sub>2</sub> Films

Z. YUAN, R. J. PUDDEPHATT and M. SAYER, *Chem. Mater.*, 1993, 5, (7), 908–910

RuO<sub>4</sub> is a good precursor for the CVD of high purity RuO<sub>2</sub> films. Films were prepared by atmospheric pressure CVD of RuO<sub>4</sub> on glass, Al and Si(100) substrates held at 150°C. The films were shiny with excellent adhesive. The resistivity of a film of 1 μm thickness is ~ 10<sup>-2</sup> Ω cm. The films were assessed for ferroelectric applications by depositing 0.3 μm thick Pb zirconate titanate films on a 1 μm thick RuO<sub>2</sub> layer. After firing and annealing the films were crack-free, crystallised in the perovskite phase, with a ferroelectric hysteresis loop.

## RuO<sub>2</sub> Films by Metal-Organic Chemical Vapor Deposition

J. SI and S. B. DESU, *J. Mater. Res.*, 1993, 8, (10), 2644–2648

An optimised hot wall MOCVD process for producing pure and conducting RuO<sub>2</sub> thin films on Si, SiO<sub>2</sub>/Si and quartz substrates at temperatures as low as 550°C was developed. Ru(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> was used as a precursor. Either pure RuO<sub>2</sub>, pure Ru or a RuO<sub>2</sub> + Ru mixture could be obtained, depending on conditions. As-deposited pure RuO<sub>2</sub> films were specular, crack-free and well adhered to the substrate. AES showed good composition uniformity across the bulk of the films.

## APPARATUS AND TECHNIQUE

### A Potentially Selective Methane Sensor Based on the Differential Conductivity Responses of Pd- and Pt-Doped Tin Oxide Thick Layers

P. DUTRONC, C. LUCAT, F. MENIL, M. LOESCH, M. C. HORRILLO, I. SAYAGO, J. GUTIERREZ and J. A. DE AGAPITO, *Sens. Actuators B*, 1993, 16, (1–3), 384–389

A sensor selective to CH<sub>4</sub> has been constructed from screen printed layers of SnO<sub>2</sub> doped with either Pt or Pd, which have different conductivities at the temperature of operation for such a device. The sensor has long-term stability and exhibits an important differential response to EtOH, which is the reverse of that for CH<sub>4</sub>. The device is insensitive to changes in relative humidity, gas flow and ambient temperature.

### Detection of Sub-ppm H<sub>2</sub>S Concentrations by Means of SnO<sub>2</sub>(Pt) Thin Films, Grown by the RGTO Technique

G. SBERVEGLIERI, S. GROPELLI, P. NELLI, C. PEREGO, G. VALDRÉ and A. CAMANZI, *Sens. Actuators B*, 1993, 15, (1–3), 86–89

The effect of Pt deposited onto the wrinkled surface of SnO<sub>2</sub> thin films grown by the RGTO (rheotaxial growth and thermal oxidation) technique was examined for detecting concentrations of 100 ppb–10 ppm H<sub>2</sub>S. A RGTO-prepared film with a layer of 35 Å Pt could detect H<sub>2</sub>S concentration of ≤ 100 ppb. The response time was 20 s and recovery time 80 s to 1 ppm H<sub>2</sub>S.

### Epitaxial Growth of Pt on Basal-Plane Sapphire: A Seed Film for Artificially Layered Magnetic Metal Structures

R. F. C. FARROW, G. R. HARP, R. F. MARKS, T. A. RABEDEAU, M. F. TONEY, D. WELLER and S. S. P. PARKIN, *J. Cryst. Growth*, 1993, 133, (1/2), 47–58

The epitaxial growth of thin ( $\leq 250$  Å) Pt films on basal-plane sapphire (0001) by molecular beam epitaxy is described. Pt nucleates as islands at 600°C, which have Pt(111)||sapphire(0001) but with two in-plane orientations related by a 180° rotation about the [111] axis. Films as thin as ~30 Å are structurally and electrically continuous and of high quality.

### Glucose Quantitation Using an Immobilized Glucose Dehydrogenase Enzyme Reactor and a Tris(2,2'-bipyridyl)ruthenium(II) Chemiluminescent Sensor

A. F. MARTIN and T. A. NIEMAN, *Anal. Chim. Acta*, 1993, 281, (3), 475–481

Glucose was detected using a flow injection analysis method. Glucose dehydrogenase was immobilised by glutaraldehyde cross-linking to pore glass to form an enzyme reactor. Ru(bpy)<sub>3</sub><sup>2+</sup> was immobilised in a Nafion film on a Pt electrode and acted as a regenerable chemiluminescent sensor. Optimum operating conditions were determined for pH ~ 6.5. The upper limit for glucose detection depends on the concentration of ( $\beta$ -nicotinamide adenine dinucleotide)' and the lower detection limit is 10  $\mu$ M glucose.

## JOINING

### Barium Titanate/Noble Metal Laminates Prepared by the Oxidation of Solid Metallic Precursors

M. M. ANTONY and K. H. SANDHAGE, *J. Mater. Res.*, 1993, 8, (11), 2968–2977

Solid metallic precursors were oxidised to produce multicomponent electronic ceramics and ceramic-metal composites for dielectric BaTiO<sub>3</sub>/Pd or Ag, laminates from Ba-Ti precursor powders. The Ba-Ti precursor was sealed in Pd or Ag tubes and rolled to form thin Ba-Ti/Pd laminates. Exposing the Ba-Ti core to  $\geq 300^\circ\text{C}$  in pure O<sub>2</sub> caused rapid oxidation, and annealing at  $\geq 900^\circ\text{C}$  gave dense BaTiO<sub>3</sub>/Pd laminates of dielectric constant 650 at room temperature and 1 kHz.

## HETEROGENEOUS CATALYSIS

### Pt-Catalyzed Combustion of CH<sub>4</sub>-C<sub>3</sub>H<sub>8</sub> Mixtures

A. BALAKRISHNA, L. D. SCHMIDT and R. ARIS, *Chem. Eng. Sci.*, 1994, 49, (1), 11–18

The effect of different amounts of C<sub>3</sub>H<sub>8</sub> on the bifurcation features of CH<sub>4</sub> catalytic combustion in air was studied over Pt foil. The behaviour can be predicted by a one-step global kinetic scheme. For some fuel ratios the system ignited directly from the extinguished state to the complete-reaction state without passing through the intermediate propane-reactive state.

### Catalysts for the Selective Dehydrogenation of High Molecular Weight Paraffins

A. A. CASTRO, *Catal. Lett.*, 1993, 22, (1, 2), 123–133  
Pt, PtSn, PtGe and PtPb catalysts supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> doped with alkaline metals were characterised and tested in *n*-decane dehydrogenation. When alkaline metals were added to Pt/Al<sub>2</sub>O<sub>3</sub>, a promoting effect on selectivity to olefins was observed. For PtSn/Al<sub>2</sub>O<sub>3</sub>-doped catalysts the performance depends on the alkaline metal used as dopant, the Sn content and the preparation method. Bimetallic catalysts give a better olefin yield and a lower selectivity to gases and aromatics than monometallic Pt catalysts.

### Surface Features and Catalytic Performance of Platinum/Alumina Catalysts in Slurry-Phase Hydrogenation

M. A. GUTIERREZ-ORTIZ, M. P. GONZÁLEZ-MARCOS, S. ARNAIZ-AGUILAR, J. A. GONZÁLEZ-MARCOS and J. R. GONZÁLEZ-VELASCO, *Ind. Eng. Chem. Res.*, 1993, 32, (11), 2457–2463

Pt catalysts supported on commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were prepared by impregnation and anionic exchange with aqueous solutions of H<sub>2</sub>PtCl<sub>6</sub>, characterised and tested for activity in the slurry-phase hydrogenation of benzene. Support type and preparation method influenced the dispersion. The activity for catalysts prepared by impregnation did not depend on the support, however, the activity of catalysts prepared by anionic exchange varied with the support. T-126 supports presented pore-diffusion problems for catalysts with higher metallic contents, due to its small average pore radius of 2.9 nm and sharp pore-size distribution.

### Stabilization and Sintering of Porous Pt/SiO<sub>2</sub>: A New Approach

W. ZOU and R. D. GONZALEZ, *Appl. Catal. A: Gen.*, 1993, 102, (2), 181–200

Pt/SiO<sub>2</sub> catalysts with well defined pore size distributions were prepared by the sol-gel method, using tetraethoxysilane (TEOS) and Pt(AcAc)<sub>2</sub> as precursors. Pore size distribution was controlled by varying the H<sub>2</sub>O:TEOS ratio during synthesis, and pores of 3.5–7.5 nm were obtained. Surface areas  $> 800$  m<sup>2</sup>/g and high Pt metal gas-phase exposure were also obtained. When particle size was matched to the average pore diameter, the resulting Pt/SiO<sub>2</sub> catalysts were structurally stable and resistant to sintering in O<sub>2</sub> at up to 675°C. To avoid sintering the metal loading was reduced to 0.2–0.3 wt. %.

### Preparation of Alumina Fiber-Type Catalyst for Methane Combustion by Sol-Gel Method

Y. MIZUSHIMA, M. SEKINE and M. HORI, *J. Ceram. Soc. Jpn.*, 1993, 101, (9), 1057–1061

Porous Al<sub>2</sub>O<sub>3</sub> fibres were prepared by the sol-gel method, and Pd was supported on the fibre by dipping or by mixing, the latter using Pd(OAc)<sub>2</sub> which was mixed with a sol before spinning. Mixing gave better dispersion of Pd particles in the fibre. The Pd/Al<sub>2</sub>O<sub>3</sub> fibre catalysts had higher activities for CH<sub>4</sub> combustion than commercial granular-type Al<sub>2</sub>O<sub>3</sub>, although the fibre had a 1/50 th smaller surface area.

### Selective Hydrogenation of Styrene on Pd-Ho/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Catalysts

V. I. PÄRVULESCU, V. PÄRVULESCU, L. FRUNZA, N. GRECU, C. ENACHE and E. ANGELESCU, *Bull. Soc. Chim. Belg.*, 1993, **102**, (6), 391–398

Pd-Ho/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts exhibit higher activity than Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for styrene hydrogenation. Adding Ho to Pd changes the place of the Pd impregnation front, depending on the state of the supported Pd. Oxidised Ho aluminate is formed as a result of the interaction between Ho and the Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support. The Ho aluminate is catalytically inactive, but represents adsorption centres for styrene. On Ho containing catalysts hydrogenation occurs between the styrene adsorbed on basic centres and H spilled from the Pd particles.

### Wacker-Type Oxidation of Cyclohexene over Palladium-Supported Heteropoly Compounds

H. SOEDA, T. OKUHARA and M. MISONO, *Nippon Kagaku Kaishi*, 1993, (8), 917–923

The liquid phase oxidation of cyclohexene by O<sub>2</sub> has been studied using Pd-supported heteropoly compounds and homogeneous catalysts. Pd-supported Cs<sub>2.5</sub>H<sub>0.5</sub>PMo<sub>6</sub>W<sub>6</sub>O<sub>40</sub> (1) was efficient for the reaction, producing cyclohexanone (Wacker-type oxidation) and cyclohexenone (allylic oxidation), while PdCl<sub>2</sub>-CuCl<sub>2</sub> had very low activity under the same conditions. Using (1), at 80°C and 8 atm of O<sub>2</sub> the turnover frequency for the total products reached ~ 25 with respect to the Pd atom, which is greater than that for a homogeneous Pd(NO<sub>3</sub>)<sub>2</sub>-H<sub>3</sub>PMo<sub>6</sub>W<sub>6</sub>O<sub>40</sub> system.

### Preparation and Catalytic Efficiency of Mixed Noble Metal Catalysts on Electrochemically Activated Carbon Fibre Supports

A. D. JANNAKOUDAKIS, P. D. JANNAKOUDAKIS, N. PAGALOS and E. THEODORIDOU, *J. Appl. Electrochem.*, 1993, **23**, (11), 1162–1168

Supported binary Ag-Pd catalysts were prepared on electrochemically activated C fibres by repetitive cation exchange between acidic groups (-COOH and -OH) and noble metal salts, followed by cathodic reduction of the exchanged metal ions to the metallic state. Catalytic efficiencies for hydrogenation of nitrobenzene in MeOH solution and nitrobenzene electroreduction were compared. The mixed Ag-Pd/C systems were more stable than double Pd-Pd/C depositions and retained their mechanical stability and catalytic activity even after prolonged storage in aqueous or methanolic solutions and after ultrasonic treatment.

### From Surface Science to Catalysis: Surface "Explosions" Observed on Rh Crystals and Supported Catalysts

T. J. CASSIDY, M. D. ALLEN, Y. LI and M. BOWKER, *Catal. Lett.*, 1993, **21**, (3,4), 321–331

Surface "explosions" for acetate species on Rh single crystals and on Rh/Al<sub>2</sub>O<sub>3</sub> catalysts under ambient pressure conditions are reported, for decomposition reactions shown by a narrow peak of 3 K wide, by TPD. The "explosions" are classed as second order autocatalytic surface processes, where free surface Rh sites and coadsorbed adatoms are essential to the reaction.

### Hydrosilylation of Alkenes Catalysed by Rhodium Complexes Immobilized on Silica via a Pyridine Group

M. CAPKA, M. CZAKOOVÁ and U. SCHUBERT, *Appl. Organomet. Chem.*, 1993, **7**, (6), 369–372

A series of Rh carbonyl complexes bound to SiO<sub>2</sub> via a pyridine group was prepared using 2-(2-trimethoxysilylethyl)pyridine and (3-methacryloxypropyl)triethoxysilane from Rh<sub>2</sub>(CO)<sub>4</sub>Cl<sub>2</sub>(Rh<sub>2</sub>). The prepared immobilised complexes were either surface-bonded or bonded in the silicate matrix. The Rh complexes efficiently catalysed the hydrosilylation of octene by triethoxysilane, and were more active than both the homogeneous analogues and complexes immobilised on organic polymers. The present catalysts suggest alternative types of immobilisation.

### Partial Oxidation of Methane over Ruthenium Catalysts

M. G. POIRIER, J. TRUDEL and D. GUAY, *Catal. Lett.*, 1993, **21**, (1,2), 99–111

The catalytic partial oxidation of CH<sub>4</sub> with O<sub>2</sub> to produce syngas was studied under various conditions over Ru supported catalysts. A catalyst with as little as 0.015 wt.% Ru/Al<sub>2</sub>O<sub>3</sub> gave a higher synthesis gas selectivity than a catalyst having 5% Ni/SiO<sub>2</sub>. Ru was produced by reduction from RuO<sub>2</sub> early during the experiments. Ru is more stable than Ni, does not form volatile carbonyl under experimental conditions, as Ni does, is less susceptible to be reoxidised during reaction and does not lead to C deposition.

### An XPS Study of Ru-Promotion for Co/CeO<sub>2</sub> Fischer-Tropsch Catalysts

M. HOANG, A. E. HUGHES and T. W. TURNEY, *Appl. Surf. Sci.*, 1993, **72**, (1), 55–65

XPS was used to examine the reduction of co-precipitated Co<sub>3</sub>O<sub>4</sub>/CeO<sub>2</sub> (1) and Ru promoted (1). The Co<sub>3</sub>O<sub>4</sub> lowered the reduction temperature of CeO<sub>2</sub>, and after reduction at 550°C, the stoichiometry of the oxide in (1) was CeO<sub>1.77 ± 0.01</sub>. Promotion with Ru lowered the reduction temperatures of both the Ce and Co constituents and a reduction of CeO<sub>2</sub> to CeO<sub>1.84 ± 0.01</sub> occurred at temperatures as low as 170°C.

## HOMOGENEOUS CATALYSIS

### Kinetics and Mechanism of Acetylene Reactions in Aqueous Iodide Solutions of Platinum. III. Hydroiodination and Reduction of Acetylene in Pt(II)-NaI-H<sup>+</sup>-H<sub>2</sub>O System

S. A. MITCHENKO, V. V. ZAMASHCHIKOV and O. N. PRYADKO, *Kinet. Katal.*, 1993, **34**, (3), 484–487

A catalytic hydroiodination and reduction of C<sub>2</sub>H<sub>2</sub> in the system Pt(II)-I-H<sup>+</sup>-H<sub>2</sub>O has been discovered; the main feature being the conversion of C<sub>2</sub>H<sub>2</sub> by  $\beta$ -iodo-platinising which forms  $\beta$ -iodovinyl Pt(II) complexes. After protolysis of Pt(II)CH=CHI vinyl iodide is formed. Another reaction with C<sub>2</sub>H<sub>2</sub> formed binuclear Pt(II)CH=CHPt(IV) compounds which were reduced by iodide ions to the  $\sigma$ -vinyl of the Pt(II), followed by protolysis of the final fraction.

### Selective Homogeneous Oxidation of Allylic Alcohols with Palladium (II) Salts

V. BELLOSTA, R. BENHADDOU and S. CZERNECKI, *Synlett*, 1993, (11), 861–863

An efficient process for the selective oxidation of allylic alcohols with PdCl<sub>2</sub> and Pd(OAc)<sub>2</sub> in the presence of other hydroxyl functional groups is described. When D-glucal was oxidised by Pd(OAc)<sub>2</sub> in the presence of NaOAc and DMF solvent for 2 h, a 95% enone yield was obtained. Testosterone was produced in good yield from steroidal allylic alcohols under similar reaction conditions. The high degree of selectivity of the reactions is explained by a fast hydride transfer from C to Pd in the allylic Pd alcoholate initially formed by ligand exchange.

### Palladium-Catalyzed Annulation of 1,4-Dienes Using *Ortho*-Functionally-Substituted Aryl Halides

R. C. LAROCK, N. G. BERRIOS-PENA, C. A. FRIED, E. K. YUM, C. TU and W. LEONG, *J. Org. Chem.*, 1993, **58**, (17), 4509–4510

The annulation of 1,4-dienes by aryl halides with *ortho*-heteroatoms and carbanion-stabilising groups, catalysed by Pd(OAc)<sub>2</sub>, gave high yields of monocyclic and bicyclic 6-membered ring heterocycles and carbocycles. The process involved aryl Pd formation and addition to the diene, Pd migration and intramolecular  $\pi$ -allyl Pd displacement.

### Hemilabile P,O-Ligands in Palladium Catalysed C-C Linkages: Codimerization of Ethylene and Styrene and Cooligomerization of Ethylene and Carbon Monoxide

G. J. P. BRITOVSEK, W. KEIM, S. MECKING, D. SAINZ and T. WAGNER, *J. Chem. Soc., Chem. Commun.*, 1993, (21), 1632–1634

Neutral and cationic Pd allyl complexes with bidentate ligands Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>CO<sub>2</sub>R (where n = 1–3) or Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>CO<sub>2</sub>R (n = 1–3; R = Me, Et) were prepared and used as catalysts for the codimerisation of C<sub>2</sub>H<sub>4</sub> and styrene, and for the co-oligomerisation of C<sub>2</sub>H<sub>4</sub> and CO. A dramatic effect for anionic as compared with neutral P,O-ligands was observed, which may be due to the hemilabile behaviour of the CO<sub>2</sub>R-group. Under catalytic conditions the O-Pd bond dissociates giving free co-ordination sites for catalysis.

### Chiral Rhodium Complex-Catalyzed Asymmetric Cyclization and Its Application to the Synthesis of Natural Products

K. SAKAI, *J. Synth. Org. Chem. Jpn.*, 1993, **51**, (8), 733–743

The Rh(I)-catalysed cyclisation of substituted 4-pentenals into cyclopentanones has been developed into a highly diastereoselective and enantioselective asymmetric cyclisation by using the Rh(I)-complex with chiral ligands, such as BINAP, and (+)-DIPMC. Cationic Rh(I) with BINAP gave the best asymmetric cyclisation in chemical yields and enantioselectivity as well as diastereoselectivity. The Rh(I) complex also catalysed the cyclisation of oct-6-enal with the *cis*-cyclohexane-1,2-dioxy function at the C3 position.

### Rhodium-Catalyzed Ring-Opening Silylformylation of Epoxides Leading to $\beta$ -Siloxy Aldehydes

Y. FUKUMOTO, N. CHATANI and S. MURAI, *J. Org. Chem.*, 1993, **58**, (16), 4187–4188

Epoxides reacted with a hydrosilane and CO in the presence of [RhCl(CO)<sub>2</sub>]<sub>2</sub> and 1-methylpyrazole, to produce a ring-opening silylformylation leading to  $\beta$ -siloxy aldehydes. The ring opening of 1-butene oxide occurred preferentially at the primary C to give a 77:23 mixture of 3-(dimethylphenylsiloxy)pentanal and 2-[(dimethylphenylsiloxy)methyl]butanal in a combined yield of 60%. An epoxide with a bulky substituent underwent a completely regioselective silylformylation.

### Rhodium Complex-Catalyzed Desilylative Cyclocarbonylation of 1-Aryl-2-(trimethylsilyl)acetylenes: A New Route to 2,3-Dihydro-1*H*-inden-1-ones

R. TAKEUCHI and H. YASUE, *J. Org. Chem.*, 1993, **58**, (20), 5386–5392

A novel cyclocarbonylation of 1-aryl-2-(trimethylsilyl)acetylene involving the C-H activation of an aromatic ring is reported during the RhCl(PPh<sub>3</sub>)<sub>3</sub>-catalysed reaction of 1-phenyl-2-(trimethylsilyl)acetylene under H<sub>2</sub>O gas shift reaction conditions, giving 2,3-dihydro-1*H*-inden-1-one (1). The products were obtained in good to excellent yield whether the substituent on the aromatic ring was electron-donating or electron-withdrawing. Various Rh complexes with excess triphenylphosphine in the presence of Et<sub>3</sub>N produced good yields of (1). A new and general synthesis of (1) is presented.

### Complete Reversal of Stereoselectivity in Rhodium Complex-Catalysed Hydrosilylation of Alk-1-yne

R. TAKEUCHI and N. TANOUCHI, *J. Chem. Soc., Chem. Commun.*, 1993, (7), 1319–1320

[Rh(cod)Cl]<sub>2</sub>-catalysed hydrosilylation of hex-1-yne with Et<sub>3</sub>SiH in EtOH or DMF is highly selective for the formation of (*Z*)-vinylsilane, whereas [Rh(cod)Cl]<sub>2</sub>-PPh<sub>3</sub> in MeCN or Pr<sup>n</sup>CN is highly selective for the formation of (*E*)-vinylsilane in 97% selectivity. The active species for *cis* addition is a Rh<sup>I</sup> cationic complex produced *in situ*.

### Effective Asymmetric Hydroboration Catalysed by a Rhodium Complex of 1-(2-Diphenylphosphino-1-naphthyl) isoquinoline

J. M. BROWN, D. I. HULMES and T. P. LAYZELL, *J. Chem. Soc., Chem. Commun.*, 1993, (22), 1673–1674

The hydroboration-oxidation reaction of vinylarenes with the title Rh catalyst gives corresponding 1-arylethanol in  $\leq 99\%$  chemoselectivity and 94% e.e. The reactions proceeded at 20°C and the best results were obtained when the Rh complex was reprecipitated before use. The result showed the potential of using chelating P-N ligands in asymmetric hydroboration, adding to their promise in Pd-catalysed allylic alkylation revealed earlier.

## Reduction of Ruthenium and Iron $\mu$ -Methylene Complexes with Hydrosilanes Producing Alkane: A Model System for Methanation *via* the Fischer-Tropsch Mechanism

M. AKITA, T. OKU, R. HUA and Y. MORO-OKA, *J. Chem. Soc., Chem. Commun.*, 1993, (22), 1670-1672

Alkane (RMe) was produced by reduction of the Ru and Fe  $\mu$ -methylene complexes  $[M_2(C_2H_5)_2(\mu-CHR)-(\mu-CO)(CO)_2]$ , where M = Ru, R = H; M = Fe, R =  $CH_2Ph$ , with hydrosilanes by way of dinuclear hydrido-methylene and methyl intermediates. This reaction sequence can be used as a model system for methanation *via* the Fischer-Tropsch mechanism.

## FUEL CELLS

### Enhanced Electrocatalysis of Oxygen Reduction on Platinum Alloys in Proton Exchange Membrane Fuel Cells

S. MUKERJEE and S. SRINIVASAN, *J. Electroanal. Chem.*, 1993, 357, (1 and 2), 201-224

The electrocatalysis of the  $O_2$  reduction reaction on some binary Pt alloys (Pt+Cr, Pt+Ni and Pt+Co) was studied at their interfaces with the PEM of perfluorinated sulphonic acids. The results, when compared to Pt/C electrocatalysts (electrodes with the same 0.3 mg/cm<sup>2</sup> Pt loading) showed enhanced activities, lower activation energies and different reaction orders for all the alloys. The alloys had lattice contractions, the predominant phase being Pt<sub>3</sub>M f.c.c. crystallite.

### An Advanced Proton Exchange Membrane Electrolyzer with an Improved Three-Dimensional Reaction Zone

K. PETROV, K. XIAO, E. R. GONZALEZ, S. SRINIVASAN, A. J. APPLEBY and O. J. MURPHY, *Int. J. Hydrogen Energy*, 1993, 18, (11), 907-913

Improved proton exchange membranes (PEM) for  $H_2O$  electrolysis, using impregnated Nafion to create a 3-dimensional reaction zone at the electrode/PEM interfaces, were studied. The anode electrocatalyst is a mixture of Ru, Ir and Ta oxide and the cathode electrocatalyst is electrodeposited Pt black on Ti and stainless steel gauze. At 85°C and current density 1 A/cm<sup>2</sup> the cell potential was 1.85 V, being constant for 1000 h. When operated as a fuel cell  $H_2$  was best oxidised at the  $Ru_3IrTaO_x$  and  $O_2$  reduced at the Pt black electrodes.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Write/Erase Cyclability of Co/Pt Disks

K. FUJIMOTO and S. HASHIMOTO, *J. Magn. & Magn. Mater.*, 1993, 126, (1-3), 587-589

The write/erase cyclic characteristics of Co/Pt disks have been studied. A disk with a quadri-layer structure (substrate|SiN 85 nm|Co/Pt 18 nm|SiN 100 nm|Al 40 nm) on a glass substrate and Curie temperature of 355°C achieved 10<sup>6</sup> write/erase cycles with a constant carrier:noise ratio.

### Reduction of Leakage Current and Minority Carrier Lifetime in Platinum-Diffused *pn* Diodes

P. SAGALA and H. KUWANO, *Jpn. J. Appl. Phys.*, 1993, 32, (9A), 3760-3763

A method to control the depth profiles of Pt-related trap concentration in Pt-diffused Si *pn* diodes and to improve their electrical properties is proposed. Pt was introduced into Si wafers and the *pn* diodes by a 1- or 2-step heat treatment. The leakage current and minority carrier lifetimes can be simultaneously minimised. With the 2-step heat treatment the trap concentrations near the surface decrease, and those in the bulk increase, to more than those of the as-diffused diodes with increased annealing temperature.

### Resistance Adjustment with Short-Pulse Nd:YAG Laser for RuO<sub>2</sub>-Based Thick-Film Resistors Buried in Polyimide Film

E. GOFUKU, T. OHNAWA, M. KOHARA and M. NUNOSHITA, *IEEE Trans. Components, Hybrids, Manuf. Technol.*, 1993, 16, (6), 592-597

The resistance of thick film resistors (TFRs) buried in polyimide film was adjusted by a new process using short-duration pulses from a Nd:YAG laser to irradiate the TFRs through the polyimide film. When a pulse optimised for duration and power density is applied to the buried TFR, the polyimide film is not degraded, but the TFR surface is modified effectively. The resistance is decreased by increasing the number of laser pulses. The modified TFR has a thin glass layer which is heavily doped with Ru impurities during the rapid thermal process.

### The Reaction between Ruthenium Dioxide and Aluminium Nitride in Resistor Pastes

C. KRETZSCHMAR, P. OTSCHIK, K. JAENICKE-RÖSSLER and D. SCHLÄFER, *J. Mater. Sci.*, 1993, 28, (21), 5713-5716  
DTA, TG, mass spectroscopy and XRD tests were performed to evaluate the reaction between RuO<sub>2</sub> and AlN in the presence of "non-reducible" glasses. RuO<sub>2</sub> can react with AlN in the presence of glass under the firing conditions used to produce thick film pastes. The reaction may cause bubbles in the resistor layers.

## TEMPERATURE MEASUREMENT

### Use of Proximity Effect in Iridium-Gold Superconducting Phase Transition Thermometers

U. NAGEL, A. NOWAK, E. KELLNER, H.-J. GEBAUER, P. COLLING, S. COOPER, D. DUMMER, P. FERGER, M. FRANK, P. FREUND, G. FORSTER, J. IGALSON, A. NUCCIOTTI, F. PRÖBST, A. RULOFS, W. SEIDEL and L. STODOLSKY, *J. Low Temp. Phys.*, 1993, 93, (3/4), 543-548

The proximity effect was used to reduce the critical temperature of Ir to below its usual value of 112.5 mK, by overlaying the Ir with Au. Measured critical temperatures for the Ir-Au bilayer films as a function of the layer thicknesses were compared to theoretical ones. Superconducting phase transition thermometers which worked in the range 30 to 100 mK were achieved.