

# ABSTRACTS

of current literature on the platinum metals and their alloys

## PROPERTIES

### Pd and Pd-Cu Bimetallic Particles Prepared by Decomposition of Organic Precursors on Clean MgO Microcrystals

S. GIORGIO, C. CHAPON and C. R. HENRY, *Langmuir*, 1997, 13, (8), 2279–2284

Pd and Pd-Cu particles have been prepared by the decomposition of acetylacetonate (acac) precursors on clean MgO microcubes. Large and small Pd particles were formed from high and low Pd(acac)<sub>2</sub> concentrations, respectively. The smaller particles had the same characteristics as those prepared by ultrahigh vacuum (UHV) condensation. Bimetallic Pd-Cu particles, formed from Pd-rich mixtures of both Pd and Cu(acac)<sub>2</sub>, were homogeneous (50%Pd-50%Cu) with ordered CsCl structure, the same as those prepared by simultaneous condensation of Pd and Cu under UHV and high-temperature annealing. However, particle densities are higher and hydride is always formed.

### Microstructural Investigation of a TiNiPd Shape Memory Thin Film

P. SCHLOSSMACHER, *Mater. Lett.*, 1997, 31, (1–2), 119–125

The microstructure of a sputter-deposited, amorphous TiNiPd thin film after crystallisation and ageing at various temperatures was studied. Crystallisation at 973–1023 K gave thin films with the desired shape memory behaviour, and the B2 matrix contained Ti<sub>2</sub>Ni(Pd) precipitates. Low-temperature crystallisation (773 K) gave brittle films and tetragonal Ti<sub>3</sub>Pd(Ni) phase particles with no shape memory behaviour.

### Nanocrystalline Structure in Pd<sub>40</sub>Ni<sub>40</sub>P<sub>20</sub> Alloy

A. ARONIN, *NanoStructured Mater.*, 1997, 8, (2), 171–177

A nanocrystalline structure with a grain size of 20–40 nm was formed in the surface layer of amorphous Pd<sub>40</sub>Ni<sub>40</sub>P<sub>20</sub> alloy when crystallisation occurred in vacuum. The surface layer was depleted in P. In situ crystallisation was also achieved by heating and annealing at 300 °C in an electron microscope column, giving structures with a grain size of 2–20 nm.

### Phase Diagram of Palladium-Rich Region in Nd-Pd-Ru Ternary System

K. ZHANG and L. CHEN, *Precious Metals (China)*, 1997, 18, (1), 4–6

The solid solubility of Ru in NdPd, was found to be up to 13 at.% on the 700°C isothermal section of the Pd-rich region of the Nd-Pd-Ru ternary phase diagram. The section consists of four single-phase regions: (Pd), (Ru), NdPd, and NbPd<sub>3</sub>; five binary-phase regions: (Pd)+(Ru), (Pd)+NdPd<sub>3</sub>, NdPd<sub>3</sub>+NdPd<sub>3</sub>, NdPd<sub>3</sub>+(Ru) and NdPd<sub>3</sub>+(Ru); and two ternary-phase regions: (Ru)+NdPd<sub>3</sub>+NdPd<sub>3</sub>, and (Pd)+(Ru)+NdPd<sub>3</sub>.

### Crystal Growth and Characterizations of ErRh<sub>3</sub>B<sub>2</sub>

T. SHISHIDO, J. YE, M. OKU, S. OKADA, K. KUDOU, T. SASAKI, T. MATSUMOTO and T. FUKUDA, *J. Alloys Compd.*, 1997, 248, 18–23

Single crystals of ternary boride ErRh<sub>3</sub>B<sub>2</sub> have been grown by the flux method using molten Cu as the solvent. ErRh<sub>3</sub>B<sub>2</sub> belongs to a monoclinic system isomorphous with ErIr<sub>3</sub>B<sub>2</sub>. The values of micro-Vickers hardness for (001) and (100) faces of the crystals are 11.3–12.0 GPa and 10.4–10.9 GPa, respectively.

### Laser Surface Alloying of Ferritic Fe-40Cr Alloy with Ruthenium

S. C. TJONG, J. S. KU and N. J. HO, *Surf. Coat. Technol.*, 1997, 90, (3), 203–209

Laser surface alloying of a Fe-40Cr stainless alloy with a Ru powder coating was studied using a continuous wave CO<sub>2</sub> laser. Microstructural studies showed that the surface alloyed layer had fine cellular dendrites with a Ru content of  $\leq$  51.84 wt.%, which greatly increased the hardness of the layer. The Ru-containing surface layer passivated spontaneously in HCl and H<sub>2</sub>SO<sub>4</sub>, while the bulk Fe-40Cr alloy remained in the active state.

## CHEMICAL COMPOUNDS

### Platinum(0)-[60]Fullerene Complexes with Chelating Diphosphine Ligands. Syntheses and Characterisation of [Pt( $\eta^2$ -C<sub>60</sub>)(L-L)] [L-L = Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>PPh<sub>2</sub>, n = 2 or 3]

M. VAN WIJNKOP, M. F. MEIDINE, A. G. AVENT, A. D. DARWISH, H. W. KROTO, R. TAYLOR and D. R. M. WALTON, *J. Chem. Soc., Dalton Trans.*, 1997, (4), 675–677

The reaction of [60]fullerene with [Pt(cod)<sub>2</sub>] (cod = cycloocta-1,5-diene) resulted in the facile displacement of the cod ligand to form black-brown insoluble PtC<sub>60</sub>. A tetrahydrofuran suspension of PtC<sub>60</sub> reacted with the bidentate diphosphines to give [Pt( $\eta^2$ -C<sub>60</sub>)(L-L)] (1) complexes via cleavage of the C-Pt bond. (1) can also be prepared in a one-pot synthesis by adding an equimolar amount of [Pt(cod)<sub>2</sub>] to a solution of [60]fullerene and diphosphine in toluene.

### Si-H and Si-C Bond Activation of a Triorganosilane Promoted by [RhCl{P(i-Pr)<sub>3</sub>}<sub>2</sub>]. Synthesis and Structure of a Dinuclear Rh(IV) Complex with $\mu$ -Silylene Ligands

K. OSAKADA, T.-A. KOIZUMI and T. YAMAMOTO, *Bull. Chem. Soc. Jpn.*, 1997, 70, (1), 189–195

The reaction of tris(2-phenylethyl)silane with [RhClL<sub>2</sub>] (L = P(i-Pr)<sub>3</sub>) in pentane gave a novel dinuclear Rh(IV) complex with bridging silylene ligands, [LRh(H)<sub>2</sub>] $\mu$ -Si(CH<sub>2</sub>CH<sub>2</sub>Ph)<sub>2</sub>]<sub>2</sub>Rh(H)<sub>2</sub>L, through Si-H and Si-C bond cleavage. A similar reaction with tribenzylsilane does not give products from Si-C bond activation.

## ELECTROCHEMISTRY

### Nitric Oxide Reduction Using Platinum Electrodes on Yttria-Stabilized Zirconia

K. J. WALSH and P. S. FEDKIW, *Solid State Ionics*, 1997, **93**, (1, 2), 17–31

Porous Pt and Pt/CeO<sub>2</sub> electrodes deposited on yttria-stabilised ZrO<sub>2</sub> (YSZ) are used to reduce electrochemically NO in inert gases at 500–600°C. The steady-state NO decomposition rate increased with temperature, NO concentration and cathodic polarisation. NO is also reduced on the Pt-based electrodes in the presence of O<sub>2</sub>, with the currents at a given electrode potential and temperature being more than an order of magnitude higher, due to simultaneous O<sub>2</sub> reduction. The yield factors, defined as the relative rate of NO reduction compared to O<sub>2</sub> reduction, are between 0.2 and 0.6 for both electrodes.

### Electrooxidation of H<sub>2</sub>/CO Mixtures on a Well-Characterized Pt<sub>75</sub>Mo<sub>25</sub> Alloy Surface

B. N. GRGUR, G. ZHUANG, N. M. MARKOVIC and P. N. ROSS, *J. Phys. Chem. B*, 1997, **101**, (20), 3910–3913

The electrochemical oxidation of H<sub>2</sub> in the presence of CO (0.05–2%) on a well-characterised Pt<sub>75</sub>Mo<sub>25</sub> alloy surface was examined using a rotating disk electrode technique in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 333 K. The shapes of the polarisation curves were remarkably similar to those for Pt<sub>50</sub>Ru<sub>50</sub> alloy, but the potential for the transition to the active state is about 0.15 V higher for the Pt<sub>75</sub>Mo<sub>25</sub> alloy. The magnitude of the current at 0.05–0.1 V, with H<sub>2</sub> containing 100 ppm CO, is high enough for the Pt-Mo alloy to have potential use as an anode catalyst in low temperature fuel cells.

### Electrocatalysis of Anodic Oxygen-Transfer Reactions: Bi<sub>3</sub>Ru<sub>3</sub>O<sub>11</sub> Electrodes in Acidic Media

L. HE, J. R. ANDERSON, H. F. FRANZEN and D. C. JOHNSON, *Chem. Mater.*, 1997, **9**, (3), 715–722

Composite materials prepared from powdered Bi<sub>3</sub>Ru<sub>3</sub>O<sub>11</sub> and a polymeric adhesive were made into disk electrodes. The materials have cubic KSbO<sub>3</sub> type structure and a composite electrode has a porous surface morphology. Oxidation occurred with transfer of O to the oxidation products in the potential region corresponding to onset of anode discharge of H<sub>2</sub>O. Mixing of Ru 4d and O 2p orbitals in an antibonding band at the Fermi level may facilitate O transfer.

### Kinetics of Oxygen Reduction at RuO<sub>2</sub>-Coated Titanium Electrode in Alkaline Solution

C.-C. CHANG and T.-C. WEN, *J. Appl. Electrochem.*, 1997, **27**, (3), 355–363

O<sub>2</sub> reduction at RuO<sub>2</sub>-coated Ti electrodes in alkaline solutions, from pH 10.8–13.8, was found to be catalysed by hydrous oxyruthenium species, Ru(III), at low polarisation (–0.1 ~ –0.45 V) and by low oxide state oxyruthenium species at high polarisation (–0.45 ~ –0.90 V). Two mechanisms for this behaviour are proposed based on measurements using a rotating disc electrode with polarisation curves, and Tafel slopes and stoichiometric number determinations.

### Reduction of Carbon Dioxide on Ruthenium Oxide and Modified Ruthenium Oxide Electrodes in 0.5 M NaHCO<sub>3</sub>

J. P. POPIĆ, M. L. AVRAMOV-IVIĆ and N. B. VUKOVIĆ, *J. Electroanal. Chem.*, 1997, **421**, (1–2), 105–110

The reduction of CO<sub>2</sub> at Ru and Ru modified by Cd and Cu adatoms was studied in 0.5 M NaHCO<sub>3</sub> solution. On the Ru surface, the modified Ru surface, and on RuOx + IrOx on Ti modified by Cu and Cd adatoms, CO<sub>2</sub> reduction yielded MeOH and acetone during 8 h when held at a constant potential of –0.8 V. The adatoms catalysed the MeOH formation, but not the acetone formation.

## PHOTOCONVERSION

### Solar Hydrogen Production Employing n-TiO<sub>2</sub>/Ti SC-SEP, Photoelectrochemical Solar Cell

M. MISRA, R. N. PANDEY and O. N. SRIVASTAVA, *Int. J. Hydrogen Energy*, 1997, **22**, (5), 501–508

A photoelectrochemical (PEC) solar cell with a new semiconductor-septum (SC-SEP) photoelectrode n-TiO<sub>2</sub>/Ti, of configuration SCE/1 M NaOH/TiO<sub>2</sub>/Ti/H<sub>2</sub>SO<sub>4</sub> + K<sub>2</sub>SO<sub>4</sub>/Pt<sub>CE</sub>, Pt<sub>WE</sub> (Pt<sub>CE</sub>, Pt<sub>WE</sub> are counter and working electrodes, respectively) was developed and used for H<sub>2</sub> production. The rate of H<sub>2</sub> production varied with electrolyte concentration in the dark compartment, the optimum rate being 13.15 l h<sup>-1</sup>m<sup>-2</sup> for 5 M H<sub>2</sub>SO<sub>4</sub>. The H<sub>2</sub> production rate for this cell was 10 times higher than for the other known n-CdSe/Ti based SC-SEP cell under optimised conditions.

### Photocatalytic Effect in Platinum Doped Titanium Dioxide Films

L. SHIVALINGAPPA, J. SHENG and T. FUKAMI, *Vacuum*, 1997, **48**, (5), 413–416

The photocatalytic activity of Pt dispersed TiO<sub>2</sub> films prepared on SiO<sub>2</sub> and a glass substrate at 200°C was studied by the decomposition of acetic acid under UV irradiation. An increase in activity was found for films containing 1.3% Pt and attributed to the formation of an anatase phase. The film morphology showed that reduction of the Pt content increased the photocatalytic effect and reduced the grain size.

### Fluorescence Properties of the Ru(bpy)<sub>3</sub><sup>2+</sup> Complex Incorporated in Sol-Gel-Derived Silica Coating Films

P. INNOCENZI, H. KOZUKA and T. YOKO, *J. Phys. Chem. B*, 1997, **101**, (13), 2285–2291

The fluorescence properties of silica gel coating films doped with Ru(bpy)<sub>3</sub><sup>2+</sup> complexes, prepared by the sol-gel method, were measured as a function of the drying temperature. The fluorescence band, resulting from the transition of metal-to-ligand charge transfer excited state to the ground state of Ru(bpy)<sub>3</sub><sup>2+</sup> showed blue shift on sol-to-gel film conversion, red shift with drying up to 200°C, and then blue shift at > 200°C. The fluorescence lifetime increased and the fluorescence efficiency decreased with increased drying temperature.

### Light-Induced Charge Separation across Ru(II)-Modified Nanocrystalline TiO<sub>2</sub> Interfaces with Phenothiazine Donors

R. ARGAZZI, C. A. BIGNOZZI, T. A. HEIMER, F. N. CASTELLANO and G. J. MEYER, *J. Phys. Chem. B*, 1997, **101**, (14), 2591–2597

Long-lived interfacial charge-separated pairs, [TiO<sub>2</sub>(e<sup>-</sup>, D<sup>+</sup>), have been created by visible light excitation of Ru(II) polypyridyl sensitizers anchored to TiO<sub>2</sub> colloids in the presence of phenothiazine donors, D. The sensitizer transfers the oxidising equivalent (the hole) away from the nanostructured semiconducting interface. The decreased electronic coupling between the surface and the hole results in a long lived (~300 μs) charge-separated pair and an increased open circuit photovoltage.

### ELECTRODEPOSITION AND SURFACE COATINGS

#### The Electrodeposition of Platinum onto a Conducting Ceramic, Ebonex<sup>®</sup>

E. E. FARNDON, D. PLETCHER and A. SARABY-REINTJES, *Electrochim. Acta*, 1997, **42**, (8), 1269–1279

The deposition of Pt from a Pt 5Q plating bath onto ceramic Ebonex<sup>®</sup>, at 368 K is described. The Ebonex<sup>®</sup> surface was pretreated by physical abrasion, polished, then chemically etched with NaF/HCl/CH<sub>3</sub>COOH solution. This gave uniform Pt coatings 0.5–2 μm thick, or with Pt loadings of 1–4 mg cm<sup>-2</sup>, which were adherent, coherent and metallic in appearance.

#### Preparation and Characterization of Pd and Pd-Ni Alloy Membranes on Porous Substrates by MOCVD with Mixed Metal β-Diketone Precursors

G. Y. MENG, L. HUANG, M. PAN, C. S. CHEN and D. K. PENG, *Mater. Res. Bull.*, 1997, **32**, (4), 385–395

A novel MOCVD process using the β-diketone precursors Pd(AcAc)<sub>2</sub> and Ni(AcAc)<sub>2</sub> has been developed to prepare Pd and Pd-Ni composite membranes on porous Al<sub>2</sub>O<sub>3</sub> ceramic substrates. This gives spindle shaped crystallites. The Pd-Ni alloy layer is gas-tight and crack free, but pinholes and cracks were detected in the Pd membrane formed from only Pd(AcAc)<sub>2</sub>.

### APPARATUS AND TECHNIQUE

#### Effect of Platinum Wire Structure on Catalytic Gas-Phase Ignition of Methane

J. G. COHN, *Fuel*, 1997, **76**, (5), 407–413

The inhibition caused by preoxidation reactions on catalytic surfaces is overcome with a new Pt catalytic igniter for CH<sub>4</sub> flames, capable of delivering thousands of ignitions. The design of this igniter mimics the dual activity principle of two-phase igniters, but achieves this in a single phase with fine Pt wire filaments. Two unexpected effects occurred: a gradual complete deactivation of Pt wire for CH<sub>4</sub> ignition by exposure to air at < 800°C, and surface migration of Pt from filament zones at > 800°C to areas at < 800°C.

#### A New Method for the Growth of Silicon Oxide Layers Below 300°C by Use of Catalytic Activity of Platinum Overlayers

H. KOBAYASHI, Y. YAMASHITA, K. NAMBA and Y. TODOKORO, *Appl. Surf. Sci.*, 1997, **108**, (4), 433–438

A new method for the growth of silicon oxide layers at low temperature (< 300°C) is described. A ~3 nm thick layer of Pt is deposited on a ~1 nm thick chemical oxide-covered Si substrate. This oxide layer effectively prevents silicide formation and Si out-diffusion, so that a Si oxide layer grows between the Pt film and the Si substrate, but is not formed on the Pt surface. After being in air at room temperature for 1 week, the oxide layer increased to ~2.6 nm, increasing to ~4.6 nm after heat treatment at 300°C in O<sub>2</sub> for 1 h.

#### Fluorescence Lifetime-Based Sensing of Methanol

Q. CHANG, J. R. LAKOWICZ and G. RAO, *Analyst*, 1997, **122**, (2), 173–177

A fluorescence lifetime-based MeOH sensor was developed by dissolving the metal-ligand fluorophore, Ru(dcbpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (where dcbpy is 4,4'-dicarboxy-2,2'-bipyridine) in poly(methyl methacrylate), which formed a thin sensing film for MeOH when cast and dried on a glass slide. When the film was removed from MeOH-free octane and placed in octane containing 2% MeOH, the fluorophore displayed a lifetime change which was monitored in the frequency domain by phase-modulating fluorimetry, using a blue LED as the excitation light source. The response time for a 95% total signal change was ~22 s.

#### Electrochemical Treatment of Low-Level Nuclear Wastes

J. O'M. BOCKRIS and J. KIM, *J. Appl. Electrochem.*, 1997, **27**, (6), 623–634

Low-level nuclear waste solutions were treated electrochemically using mass-transfer controlled reductions of Hg(II), [RuNO(NO<sub>2</sub>)<sub>2</sub>OH]<sup>2+</sup> and CrO<sub>4</sub><sup>2-</sup> and the activation controlled reduction of NO<sub>3</sub><sup>-</sup> in the presence of NaOH, at packed bed electrodes. Based on the data obtained, this process is economically favourable and scale-up for each reduction is proposed. A plant design and detailed calculations for this are presented. This process can also be made to produce, as by-products, HNO<sub>3</sub> and NaOH.

#### Oxidation of Guanine in DNA by Ru(phen)<sub>2</sub>(dppz)<sup>3+</sup> Using the Flash-Quench Technique

E. D. A. STEMPEL, M. R. ARKIN and J. K. BARTON, *J. Am. Chem. Soc.*, 1997, **119**, (12), 2921–2925

A flash-quench method to probe oxidative damage to DNA is presented. A photoexcited intercalator, Ru(phen)<sub>2</sub>(dppz)<sup>3+</sup> (dppz = dipyrrophenazine) is quenched in DNA by a weakly bound, electron-transfer quencher to generate Ru(III), a powerful ground-state oxidant. This binds to poly(dG-dC) and rapidly oxidises guanine to a radical species. Oxidative damage is a major pathway for decay of the radical and the quantum yield can be tuned by choice of quencher.

## HETEROGENEOUS CATALYSIS

### Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Catalytic Membranes vs. Pt on $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Powders in the Selective Hydrogenation of *p*-Chloronitrobenzene

G. VITULLI, A. VERRAZZANI, E. PITZALIS, P. SALVADORI, G. CAPANNELLI and G. MARTRA, *Catal. Lett.*, 1997, 44, (3, 4), 205–210

Using Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalytic membranes, the hydrogenation of *p*-chloronitrobenzene in EtOH yielded *p*-chloroaniline as the only reaction product, while Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder systems gave a complex mixture of products, under the same reaction conditions. This difference is attributed to the Pt/membrane reactor supplying more H<sub>2</sub> to the system.

### Isomerization and Hydrocracking of Heptane Over Bimetallic Bifunctional PtPd/H-Beta and PtPd/USY Zeolite Catalysts

E. BLOMSMA, J. A. MARTENS and P. A. JACOBS, *J. Catal.*, 1997, 165, (2), 241–248

Bimetallic bifunctional PtPd/H-Beta zeolite catalysts were found to be more active and selective in the isomerisation of heptane than monometallic Pd/H-Beta and Pt/H-Beta zeolites. This was due to the improved dispersion of the Pt in the presence of as little as 20 mole% of Pd, leading to a better intimacy and balance of the acid and hydrogenation-dehydrogenation functions. Undesired hydrogenolysis and dimerisation-cracking were also suppressed. Similar effects were seen with USY zeolites.

### Conversion of *n*-Hexane over Pt-Sn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Catalyst

P. KIRSZENSZTEJN and L. WACHOWSKI, *React. Kinet. Catal. Lett.*, 1997, 60, (1), 93–99

The effect of the preparation of Pt-Sn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts on physicochemical properties was studied during conversion of *n*-hexane. Sn was found to modify the acidity of the support and to alter the local density of states at surface Pt atoms, reducing self-poisoning and selectivity for the non-destructive reaction. Catalysts obtained by co-precipitation were much more stable than those where Sn was added by impregnation, although activity was not greatly affected.

### Effect of Carbonate Salt Addition on the Photocatalytic Decomposition of Liquid Water over Pt-TiO<sub>2</sub> Catalyst

K. SAYAMA and H. ARAKAWA, *J. Chem. Soc., Faraday Trans.*, 1997, 93, (8), 1647–1654

The stoichiometric photocatalytic decomposition of liquid H<sub>2</sub>O into H<sub>2</sub> and O<sub>2</sub> is demonstrated over Pt-TiO<sub>2</sub> suspensions upon the addition of carbonate salts. A high concentration of HCO<sub>3</sub><sup>-</sup> or CO<sub>3</sub><sup>2-</sup> anions was needed, as well as a pH of 8–11.5 (optimum 10.6), a Pt loading of around 0.3 wt.% and a low total pressure in the reactor. The Pt-TiO<sub>2</sub> surface became covered with several carbonate species which appeared to reduce the rate at which H<sub>2</sub> and O<sub>2</sub> recombine to form H<sub>2</sub>O on the Pt, as well as aid desorption of O<sub>2</sub> from the TiO<sub>2</sub> surface. A new reaction mechanism involving peroxocarbonate species is proposed.

### 1,3-Butadiene Hydrogenation on Pd<sub>50</sub>Cu<sub>50</sub> Single Crystals

L. LIANOS, Y. DEBAUGE, J. MASSARDIER, Y. JUGNET and J. C. BERTOLINI, *Catal. Lett.*, 1997, 44, (3, 4), 211–216

The catalytic properties of (111) and (110) Pd<sub>50</sub>Cu<sub>50</sub> single-crystal surfaces were studied during 1,3-butadiene hydrogenation and compared to those of pure Pd with the same surface orientation. Activity was enhanced despite the lower number of Pd sites, due to a “positive” electronic ligand effect from surrounding Cu atoms on the active Pd surface atoms. The activity of the PdCu(111) single crystal was 8 times higher than that of the PdCu(110). The results are discussed in terms of geometric and electronic effects.

## HOMOGENEOUS CATALYSIS

### Transition Metal Nanoparticles Protected by Amphiphilic Block Copolymers as Tailored Catalyst Systems

A. B. R. MAYER and J. E. MARK, *Colloid Polym. Sci.*, 1997, 275, (4), 333–340

A number of stable Pd, Pt, Ag and Au colloids were prepared by reducing the corresponding metal precursors, such as PdCl<sub>2</sub>, Pd(CH<sub>3</sub>COO)<sub>2</sub>, H<sub>2</sub>PtCl<sub>6</sub> and Pt(CH<sub>3</sub>COCH=C(O-)-CH<sub>3</sub>)<sub>2</sub>, in the presence of protective amphiphilic block copolymers, such as polystyrene-*b*-poly(ethylene oxide), etc. The protected Pd and Pt nanoparticles were found to be catalytically active in the hydrogenation of cyclohexene, giving  $\leq$  100% cyclohexane. Activities can be tailored by varying the polymer block types and lengths, the precursor type and the reduction method.

### Regioselective Synthesis of 1,3,5-Unsymmetrically Substituted Benzenes via the Palladium-Catalyzed Cyclotrimerization of 1,3-Diynes

A. TAKEDA, A. OHNO, I. KADOTA, V. GEVORGYAN and Y. YAMAMOTO, *J. Am. Chem. Soc.*, 1997, 119, (19), 4547–4548

The regioselective synthesis of 1,3,5-trisubstituted benzenes via the Pd-catalysed trimerisation of 1,3-diynes is reported. Using the catalytic systems Pd(dba)<sub>2</sub> (5 mol%)/PPh<sub>3</sub> (20 mol%) and Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol%), 3 different substituents can be introduced at the 1-, 3- and 5-positions, leading to the synthesis of novel aromatic compounds not otherwise readily available.

### Carbonylation of Methanol Catalyzed by Polymer-Protected Rhodium Colloid

Q. WANG, H. LIU, M. HAN, X. LI and D. JIANG, *J. Mol. Catal. A: Chem.*, 1997, 118, (2), 145–151

Poly(*N*-vinyl-2-pyrrolidone)(PVP) protected Rh colloid (Rh-PVP) was used as a catalyst for MeOH carbonylation under elevated temperature (140°C) and high pressure (5.4 MPa). The catalyst remained in a colloidal state, and its activity increased after being recycled 6 times for 56.5 h, with total turnover number reaching 19,700 cycles/atom Rh. The Rh-PVP colloid partially changed to [Rh(CO)<sub>2</sub>I<sub>2</sub>] during the reaction, due to the oxidative addition of MeI.

### Selective Tail-to-Tail Dimerization of Ethyl Acrylate Catalyzed by Dirhodium Complexes

Y. KANEKO, T. KANKE, S.-I. KIYOOKA and K. ISOBE, *Chem. Lett. Jpn.*, 1997, (1), 23–24

A catalytic selective tail-to-tail dimerisation of ethyl acrylate was achieved using dinuclear Rh complexes,  $[(\text{RhCp}^*)_2(\mu\text{-CH}_2)_2(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$  ( $\text{Cp}^* = \text{C}_5\text{Me}_5$ ) and  $[(\text{RhCp}^*)_2(\mu\text{-CH}_2)_2(\text{CO})_2](\text{BF}_4)_2$ . The corresponding dimethyl complex  $[(\text{RhCp}^*)_2(\mu\text{-CH}_2)_2(\text{CH}_3)_2]$  was only catalytic in the presence of  $\text{HBF}_4 \cdot \text{OEt}_2$ .

### Highly Selective Allylic Alkylation with a Carbon Nucleophile at the More Substituted Allylic Terminus Catalyzed by an Iridium Complex: An Efficient Method for Constructing Quaternary Carbon Centres

R. TAKEUCHI and M. KASHIO, *Angew. Chem., Int. Ed. Engl.*, 1997, 36, (3), 263–265

A high yielding (70–85%), 100% selective method for the allylic alkylation of acyclic systems with C nucleophiles, catalysed by  $[\text{Ir}(\text{cod})\text{Cl}]_2$  (cod = cyclooctadiene) in the presence of P ligands is reported.  $\text{P}(\text{OPh})_3$  is the most effective ligand. The regioselectivity is opposite to that achieved with Pd catalysts.

### Evidence for Living Radical Polymerization of Methyl Methacrylate with Ruthenium Complex: Effects of Protic and Radical Compounds and Reinitiation from the Recovered Polymers

T. NISHIKAWA, T. ANDO, M. KAMIGAITO and M. SAWAMOTO, *Macromolecules*, 1997, 30, (8), 2244–2248

The effects of additives, such as MeOH,  $\text{H}_2\text{O}$ , and radical scavengers (TEMPO and galvinoxyl) were studied on  $\text{PhCOCHCl}_2/\text{RuCl}_2(\text{PPh}_3)_3/\text{Al}(\text{O}i\text{Pr})_3$ , catalysed living polymerisation of methyl methacrylate in toluene at 80°C. When the additives were added at ~45% conversion, TEMPO and galvinoxyl completely terminated the polymerisation, but  $\text{H}_2\text{O}$  and MeOH concentration did not affect it. Living polymerisation proceeds via a radical pathway and the polymer terminal is robust, but generates an active end in the presence of the Ru and Al compounds.

### Two-Phase Catalytic Hydrogenation of Olefins by Ru(II) and Co(II) Complexes Dissolved in 1-*n*-Butyl-3-Methylimidazolium Tetrafluoroborate Ionic Liquid

P. A. Z. SUAREZ, J. E. L. DULLIUS, S. EINLOFT, R. F. DE SOUZA and J. DUPONT, *Inorg. Chim. Acta*, 1997, 255, (1), 207–209

The interaction of  $\text{RuCl}_2(\text{PPh}_3)_3$  with 1-*n*-butyl-3-methylimidazolium tetrafluoroborate molten salt gives an air and  $\text{H}_2\text{O}$  stable solution that can hydrogenate olefins with turnover frequencies (TOFs) of up to 537  $\text{h}^{-1}$  in a typical 2-phase catalytic system. These TOFs are generally higher than those obtained from classical catalysts based on  $\text{H}_2\text{O}$ -soluble phosphane transition metal complexes which require the use of more drastic conditions and cosolvents. The products can be easily separated from the reaction mixtures and the catalysts reused  $\geq 4$  times without loss of efficiency.

### Ruthenium Complex-Catalyzed Synthesis of Indoles from *N*-Substituted Anilines and Alkanolamines

D. Y. LEE, C. S. CHO, J. H. KIM, Y. Z. YOUN, S. C. SHIM and H. SONG, *Bull. Korean Chem. Soc.*, 1996, 17, (12), 1132–1135

*N*-Substituted anilines reacted with triethanolamine, *N*-benzyl-diethanolamine or triisopropanolamine at 180°C in the presence of a catalytic amount of  $\text{RuCl}_2(\text{PPh}_3)_3$  to give the corresponding 1-substituted indoles in good to high yields. An intermolecular alkyl group transfer between anilines and alkanolamines is proposed as the key step in these reactions.

### Regio- and Stereo-Selective Oxidation of Steroids Using 2,6-Dichloropyridine *N*-Oxide Catalysed by Ruthenium Porphyrins

T. SHINGAKI, K. MIURA, T. HIGUCHI, M. HIROBE and T. NAGANO, *Chem. Commun.*, 1997, (9), 861–862

The oxidation of various steroids with 2,6-dichloropyridine *N*-oxide was catalysed by the porphyrins,  $\text{Ru}(\text{TPP})\text{CO}$ ,  $\text{Ru}(\text{TMP})\text{CO}$  and  $\text{Ru}(\text{TDCIPP})\text{CO}$ , in HBr. The reactions proceeded with retention of configuration at the asymmetric centres giving novel steroids. The regioselectivity depended strongly on the steric and electronic effects of substituents on the porphyrins.

## FUEL CELLS

### High Performance Proton Exchange Membrane Fuel Cells with Sputter-Deposited Pt Layer Electrodes

S. HIRANO, J. KIM and S. SRINIVASAN, *Electrochim. Acta*, 1997, 42, (10), 1587–1593

An ultra-low Pt loading (0.1  $\text{mg cm}^{-2}$ ) electrocatalyst layer (1  $\mu\text{m}$  thick) has been deposited on an uncatalysed gas diffusion electrode by sputter deposition. A PEMFC with this electrode for the cathode showed a good  $\text{O}_2$  electrode performance, even at high current densities, comparable to that of a standard E-TEK electrode (20% Pt/C, 0.4  $\text{mg Pt cm}^{-2}$ ), but lower than the above with a sputtered Pt layer. Cell performance was, however, lower due to high anode overpotentials at higher current densities.

### Electrocatalytic Activity of PtRu Alloy Colloids for CO and $\text{CO}/\text{H}_2$ Electrooxidation: Stripping Voltammetry and Rotating Disk Measurements

T. J. SCHMIDT, M. NOESKE, G. A. GASTEIGER, R. J. BEHM, P. BRITZ, W. BRIJOUX and H. BÖNNEMANN, *Langmuir*, 1997, 13, (10), 2591–2595

The coreduction of  $\text{PtCl}_2$  and  $\text{RuCl}_2$  by tetraalkylammonium hydrotriethylborate in THF leads to a colloidal PtRu alloy of the form  $\text{Pt}_{0.5}\text{Ru}_{0.5}$ , with a mean particle size diameter of  $1.7 \pm 0.5$  nm. CO-stripping voltammetry data for glassy C supported  $\text{Pt}_{0.5}\text{Ru}_{0.5}$  clusters was comparable to that for well-characterised bulk alloy electrodes. The activity of the colloid towards the continuous oxidation of 2% CO in  $\text{H}_2$  indicates that PtRu colloids may be used for the preparation of bimetallic high-surface-area fuel cell catalysts.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Investigation of Pt/Ti Bottom Electrodes for Pb(Zr,Ti)O<sub>3</sub> Films

S.-T. KIM, H.-H. KIM, M.-Y. LEE and W.-J. LEE, *Jpn. J. Appl. Phys.*, 1997, 36, (1), 294–300

Pt films, used as bottom electrodes for PZT capacitors, were deposited on Ti/SiO<sub>2</sub>/Si substrates by DC magnetron sputtering. The structure and electrical properties of the PZT films depended strongly on the deposition conditions of the Pt film. As the deposition temperature of the Pt film increased and the deposition rate decreased, the film became dense, and Ti out-diffusion and film deformation were suppressed. At high temperature, Ti diffused through the grain boundary of the Pt overlayer, to form nucleation sites for the perovskite PZT films.

### The Optimization of the Double Mask System to Minimize the Contact Resistance of a Ti/Pt/Au Contact

G. L. WAYTENA, H. A. HOFF, I. P. ISAACSON, M. L. REBBERT, D. I. MA, C. MARRIAN and J. S. SUEHLE, *J. Electron. Mater.*, 1997, 26, (2), 90–96

Fabrication of Ti/Pt/Au ohmic contacts on diamond was modified to minimise adverse effects from the rectifying lip (1) and surface O<sub>2</sub> contributions on resistance. (1) was decreased by diffusing Ti from below the contact defined by the first mask, and decreasing the overlap of the two masks from 5 to 2 μm. O<sub>2</sub> was desorbed from the diamond surface by heating in vacuum then cooling in H<sub>2</sub>. Contact resistance dropped from  $8.1 \times 10^{-2} \Omega \text{ cm}^2$  to  $1.2 \times 10^{-4} \Omega \text{ cm}^2$ .

### Pt/Ti/Pt/Au Schottky Contacts on InGaP/GaAs HEMTs

J. R. LOTHIAN, F. REN, J. M. KUO, J. S. WEINER and Y. K. CHEN, *Solid-State Electron.*, 1997, 41, (5), 673–675

The electrical characteristics of Pt/Ti/Pt/Au based Schottky (1) contacts on InGaP/GaAs HEMT devices and the effect of annealing were studied. (1) has a higher relative barrier height and a higher turn-on voltage than the standard Ti/Pt/Au and Mo/Ti/Pt/Au Schottky contacts and is dependent upon Pt thickness. Annealing at 200°C for 10 min raises the voltage for the Pt-based contact to 0.85 V. A 50 Å Pt metallisation gives the highest turn-on and reverse breakdown voltages, good adhesion and thermal stability.

### Electrical and Structural Characterization of PtSi/p-Si<sub>1-x</sub>Ge<sub>x</sub> Low Schottky Barrier Junctions Prepared by Co-sputtering

O. NUR, M. WILLANDER, R. TURAN, M. R. SARDELA, H. H. RADAMSON and G. V. HANSSON, *J. Vac. Sci. Technol. B*, 1997, 15, (2), 241–246

Schottky barrier junctions of PtSi/Si<sub>1-x</sub>Ge<sub>x</sub> were produced. The silicide was co-sputtered on defect-free well-calibrated strained Si<sub>1-x</sub>Ge<sub>x</sub> (1) ( $0 \leq x \leq 0.242$ ) layers. The barrier height of the junctions with Ge fraction  $x$  was found to decrease by a similar amount as the band gap of strained (1).

### Perpendicular Magnetic Anisotropy and Magneto-optical Properties of (Co<sub>1-x</sub>Ni<sub>x</sub>)/Pd Multilayers

J.-G. HA, K. KYUNO and R. YAMAMOTO, *IEEE Trans. Magn.*, 1997, 33, (2), 1049–1051

Studies of magnetic and magneto-optical properties of (Co<sub>1-x</sub>Ni<sub>x</sub>)/Pd multilayers showed that addition of Ni to the Co layer simultaneously decreases the Curie temperature and Kerr rotation angle, but the decrease in the Curie temperature is larger. The perpendicular magnetic anisotropy energy also decreases, but by a small amount. It is suggested that the magnetic and magneto-optical properties can be controlled by adding Ni to the Co layer, while maintaining a large effective perpendicular anisotropy energy.

### Performance of Pd-Ge Based Ohmic Contacts to n-Type GaAs

D. G. IVEY, S. EICHER, S. WINGAR and T. LESTER, *J. Mater. Sci., Mater. Electron.*, 1997, 8, (2), 63–68

The performance of Pt-Ge based ohmic contacts, with and without Ti-Pt or Ti-Pt-Au capping layers, was studied. The capped contacts had a nearly 3-fold superior contact resistance, which is attributed to the capping layers protecting the Pd-Ge layers during contact processing. No change in contact resistance was seen after 1350 h at 235°C, but a 7-fold increase after ageing at 290°C for 370 h was attributed to interdiffusion between Ge and GaAs, and not to phase changes.

## MEDICAL USES

### Synthesis, Characterization and Antitumor Activity of Platinum Triamine Complexes Containing Imidazothiazole Ligands

C. L. BAIRD, A. E. GRIFFITHS, S. BAFFIC, P. BRYANT, B. WOLF, J. LUTTON, M. BERARDINI and G. M. ARVANITIS, *Inorg. Chim. Acta*, 1997, 256, (2), 253–262

A series of Pt(II) and Pt(IV) cationic cisplatin analogues of the form [PtA<sub>2</sub>(N-het)Cl]<sup>+</sup> or [PtA<sub>2</sub>(N-het)Cl]<sub>2</sub><sup>+</sup> (A = NH<sub>2</sub>, or A<sub>2</sub> = ethylenediamine; N-het = an imidazothiazole or a derivative) have been prepared. Biological screening showed that the compounds with *cis* ammine groups are more active than those with a *trans* arrangement. Complexes with ligands derived from benzimidazole moieties showed promising cytotoxicity in vitro and Pt(IV) derivatives were found to be at least as active as their Pt(II) analogues.

### Effects of Palladium on the Thermal Behavior of the γ<sub>1</sub>-Phase of the Ag-Sn-Cu Dental Amalgam

E. HERDA, R. HIGUCHI-RUSLI and PARANGTOPO, *Mater. Lett.*, 1997, 30, (5, 6), 347–350

Effects of the addition of 1 wt.% Pd on the thermal behaviour of a lathe-cut type of high Cu amalgam were studied on two alloys containing (in wt.%): 60 Ag–27 Sn–13 Cu and 59 Ag–27 Sn–13 Cu–1 Pd. The addition of 1 wt.% Pd produced a more thermally stable dental amalgam by eliminating the formation of a γ<sub>2</sub>-phase and stabilising and homogenising the distribution of Sn in the γ<sub>1</sub>-phase.