

# ABSTRACTS

of current literature on the platinum metals and their alloys

## PROPERTIES

### The Stabilization of Pt<sub>3</sub>Al Phase with L1<sub>2</sub> Structure in Pt–Al–Ir–Nb and Pt–Al–Nb Alloys

C. HUANG, Y. YAMABE-MITARAI and H. HARADA, *J. Alloys Compd.*, 2004, 366, (1–2), 217–221

The structure of the Pt<sub>3</sub>Al phase in the title alloys was investigated using SEM, XRD, DTA and TEM techniques. The alloys were prepared using pure metal powders by an arc-melting method in an Ar atmosphere. The structure form was determined to be cubic L1<sub>2</sub>. The stabilisation of the L1<sub>2</sub>-Pt<sub>3</sub>Al structure at room temperature was due to the effect of Nb.

### Phase Transformation and Magnetic Anisotropy of an Iron–Palladium Ferromagnetic Shape-Memory Alloy

J. CUI, T. W. SHIELD and R. D. JAMES, *Acta Mater.*, 2004, 52, (1), 35–47

The f.c.c.-f.c.t. transformation in Fe<sub>7</sub>Pd<sub>3</sub> is a weak first-order thermoelastic transition. The latent heat of the f.c.c.-f.c.t. transformation is  $10.79 \pm 0.01$  J cm<sup>-3</sup>. Magnetic measurements indicate the tetragonal martensitic phase has easy axes in the [1 0 0] and [0 1 0] (*a*-axes) directions while [0 0 1] (*c*-axis) is the hard direction.

### Microstructure and Mechanical Properties of

#### Ru–Al–Mo Alloys

T. D. REYNOLDS and D. R. JOHNSON, *Intermetallics*, 2004, 12, (2), 157–164

Alloys in the Ru–Al–Mo system were produced by arc-melting and a cold crucible Czochralski technique. One set of alloys consisted of eutectic microstructures between RuAl and a b.c.c. (Mo, Ru) solid solution. The other set of alloys consisted of RuAl and a h.c.p. (Ru, Mo) solid solution; a change from eutectic to peritectic solidification occurs as the Mo concentration increases. The RuAl–h.c.p. (Ru, Mo) eutectic microstructure was found to consist of RuAl fibres embedded in a (Ru, Mo) matrix.

## CHEMICAL COMPOUNDS

### Synthesis, Structure, and Reactivity of Arylfluoro Platinum(II) Complexes

P. NILSSON, F. PLAMPER and O. F. WENDT, *Organometallics*, 2003, 22, (25), 5235–5242

*trans*-[PtPhFL<sub>2</sub>] (L = PPh<sub>3</sub> (1) and PMe<sub>2</sub>Ph (2)) were synthesised and then (1) was characterised by X-ray crystallography. The equilibrium constant for the substitution of F<sup>-</sup> *trans* to phenyl in (1) by Cl<sup>-</sup> and I<sup>-</sup> was determined. The Pt has preference for the halide: I > Cl > F. (1) and (2) reacted with Me<sub>3</sub>SnPh within 2–15 min. (1) gave *trans*-[PtPhMe(PPh<sub>3</sub>)<sub>2</sub>], whereas (2) gave *trans*-[PtPhMe(PMe<sub>2</sub>Ph)<sub>2</sub>] and *trans*-[PtPh<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>].

### Gas-Phase Studies on the Reactivity of the Azido(diethylenetriamine)platinum(II) Cation and Derived Species

S. WEE, J. M. WHITE, W. D. MCFADYEN and R. A. J. O'HAIR, *Aust. J. Chem.*, 2003, 56, (12), 1201–1207

Collision-induced dissociation and ion–molecule reactions of [Pt(dien)N]<sup>+</sup> (1) were carried out in the gas phase. Labelling studies (<sup>15</sup>N and <sup>2</sup>H labelling of the dien ligand) were also employed. The H atoms of both the amino groups and the C backbone of the dien ligand are involved in loss of NH<sub>3</sub> from (1). The crystal structure of [Pt(dien)<sub>3</sub>]<sup>+</sup> was also determined.

### Coordination of Amines to Palladium(II) Complexes of N<sup>21</sup>, N<sup>22</sup>-Bridged Porphyrins

Y. TAKAO, T. TAKEDA and J. SETSUNE, *Bull. Chem. Soc. Jpn.*, 2003, 76, (8), 1549–1553

Pyridine and ethylenediamine (en) reacted with the title Pd(II) porphyrins to give mixed-ligand Pd(II) complexes. The splitting pattern in the Soret region of their UV-vis spectra was dependent on whether the porphyrinato Pd(II) was coordinated by neutral ligands or anionic ligands. In the <sup>1</sup>H NMR spectra of en complexes of porphyrinato Pd(II), signal broadening of porphyrin β-pyrrole protons and a chemical shift change of en protons were seen in the dichloride in comparison with the bis(perchlorate).

### Synthesis and Reactivity of Bucky Ruthenocene

#### Ru(η<sup>5</sup>-C<sub>60</sub>Me<sub>5</sub>)(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)

Y. MATSUI, Y. KUNINOBU, S. ITO and E. NAKAMURA, *Chem. Lett.*, 2004, 33, (1), 68–69

Metathetical coupling of Ru(η<sup>5</sup>-C<sub>60</sub>Me<sub>5</sub>)Cl(CO)<sub>2</sub> and CpNa resulted in a molecular hybrid of ruthenocene and fullerene: Ru(η<sup>5</sup>-C<sub>60</sub>Me<sub>5</sub>)(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>) (1). In (1), the bonding between the Ru atom and the C<sub>60</sub>Me<sub>5</sub> ligand as well as between the metal atom and the Cp group is very different from that of known ferrocene and ruthenocene compounds. (1) is quite reactive compared to the rather stable bucky ferrocene compound.

### Specific Heat of Sr<sub>4</sub>Ru<sub>3</sub>O<sub>10</sub>

X. N. LIN, V. A. BONDARENKO, G. CAO and J. W. BRILL, *Solid Commun.*, 2004, 130, (3–4), 151–154

A flux grown (FG) sample of Sr<sub>4</sub>Ru<sub>3</sub>O<sub>10</sub> (1) had a sharp mean-field-like anomaly at the onset of magnetic order, T<sub>c</sub> = 102 K, but a much broader anomaly, indicative of residual heterogeneity, was observed for an image furnace grown sample. Even for the FG sample, however, the anomaly was at least an order of magnitude smaller than would be expected for complete ordering of the spins. Neither sample exhibited an anomaly at T<sub>M</sub> ~ 50 K. Anomalous behaviour was observed at low temperatures for both samples, indicative of the unusual magnetic order in (1).

## ELECTROCHEMISTRY

### **IrO<sub>2</sub>/SnO<sub>2</sub> Electrodes: Prepared by Sol-Gel**

**Process and Their Electrocatalytic for Pyrocatechol**  
Y. LIU, Z. LI and J. LI, *Acta Mater.*, 2004, 52, (3), 721–727

IrO<sub>2</sub>/SnO<sub>2</sub> (10%/90%, molar ratio) electrodes (1) were prepared by the sol-gel method. Oxide films prepared at low temperature were in an amorphous state, while hydrous IrO<sub>2</sub> crystal and cassiterite phase SnO<sub>2</sub> were formed at 300°C or even to 500°C. (1) with the highest electroactivity were formed at 400°C. For the electrocatalysis of pyrocatechol on (1), a quasi-reversible process occurred. The detection limit of pyrocatechol was  $5 \times 10^{-3}$  mM.

### **NiO-Based Composite Electrode with RuO<sub>2</sub> for Electrochemical Capacitors**

X. M. LIU and X. G. ZHANG, *Electrochim. Acta*, 2004, 49, (2), 229–232

NiO/RuO<sub>2</sub> composite materials were prepared by the coprecipitation method followed by heat treatment. XRD spectra indicated that the Ru oxide particles were coated by NiO particles. RuO<sub>2</sub> partly introduced into NiO-based electrodes improved their electrochemical performance and capacitive properties. A maximum specific capacitance of 210 F g<sup>-1</sup> was achieved for a NiO-based composite electrode with 10 wt.% RuO<sub>2</sub> at -0.4 to 0.5 V in 1 mol l<sup>-1</sup> KOH solution. Chemically modified composite electrodes had more stable cycling properties than those of physically modified electrodes.

## PHOTOCONVERSION

### **The Photohydrochlorination of Platinum(IV) Chloride in Chloroform**

P. E. HOGGARD, A. J. BRIDGEMAN, H. KUNKELY and A. VOGLER, *Inorg. Chim. Acta.*, 2004, 357, (3), 639–643

When irradiated by light at 240 nm, PtCl<sub>4</sub> in CHCl<sub>3</sub> was converted to H<sub>2</sub>PtCl<sub>6</sub> via a Pt(V) intermediate. When irradiated by light at > 265 nm, PtCl<sub>4</sub> was converted to H<sub>2</sub>PtCl<sub>4</sub> and H<sub>2</sub>PtCl<sub>6</sub> in equal amounts. At > 265 nm, the reaction may proceed by Cl dissociation from a LMCT excited state of Pt(IV), through a Pt(III) intermediate.

### **Multicolored Electrogenenerated Chemiluminescence from Ortho-Metalated Iridium(III) Systems**

B. D. MUEGGE and M. M. RICHTER, *Anal. Chem.*, 2004, 76, (1), 73–77

Bis(3,5-difluoro-2-(2-pyridyl)phenyl-(2-carboxypyridyl))-Ir(III), F(Ir)pic, is a blue emitter ( $\lambda_{\text{ECL}} \sim 470$  nm) and bis[2,(2'-benzothienyl)pyridinato-N,C3'](acetylacetonate)Ir(III), (btp)<sub>2</sub>Ir(acac), emits in the red ( $\lambda_{\text{ECL}} \sim 600$  nm). The ECL solution spectrum of each complex is identical to its photoluminescence spectrum, indicating the same metal-to-ligand excited states. The oxidative reductive coreactant tri-*n*-propylamine was used. ECL intensity increased in the presence of Triton X-100 surfactant: up to 6-fold for F(Ir)pic and up to 20-fold for (btp)<sub>2</sub>Ir(acac).

### **Enhanced Electrochemiluminescence from Os(phen)<sub>2</sub>(dppene)<sup>2+</sup> (phen = 1,10-phenanthroline and dppene = bis(diphenylphosphino)ethene) in the Presence of Triton X-100 (Polyethylene Glycol tert-Octylphenyl Ether)**

J. WALWORTH, K. J. BREWER and M. M. RICHTER, *Anal. Chim. Acta*, 2004, 503, (2), 241–245

The anodic oxidation of Os(phen)<sub>2</sub>(dppene)<sup>2+</sup> produced electrochemiluminescence (ECL) in the presence of tri-*n*-propylamine (TPrA) in aqueous surfactant solution. Increases in ECL efficiency ( $\geq 3$ -fold) and TPrA oxidation current ( $\geq 2$ -fold) were observed in Triton X-100 surfactant media. Experiments indicated adsorption of surfactant on the electrode surface.

### **Can Clay Emit Light? Ru(bpy)<sub>3</sub><sup>2+</sup>-Modified Clay Colloids and Their Application in the Detection of Glucose**

P. Y. LIANG, P. W. CHANG and C. M. WANG, *J. Electroanal. Chem.*, 2003, 560, (2), 151–159

Electrochemical-quartz-crystal-microbalance techniques showed that Ru(bpy)<sub>3</sub><sup>3+</sup> can be adsorbed by montmorillonite K10 clay colloids. The resulting clay particles (1) emitted light ( $\lambda_{\text{em}} = 610$  nm) when they were fabricated as thin films sandwiched by two conductive ITO electrodes with opposite biases. A glucose optrode was fabricated using (1) and glucose oxidase. The electrochemiluminescence signals behaved as a function of [glucose]: 0.1–10 mM at pH 10. At this pH, the detection limit reached 0.1 mM.

### **Photoelectrochemical Properties of Supramolecular Species Containing Porphyrin and Ruthenium Complexes on TiO<sub>2</sub> Films**

A. F. NOGUEIRA, A. L. B. FORMIGA, H. WINNISCHOFER, M. NAKAMURA, F. M. ENGELMANN, K. ARAKI and H. E. TOMA, *Photochem. Photobiol. Sci.*, 2004, 3, (1), 56–62

Supramolecular species based on porphyrin and Ru(II) polypyridyl complexes were used as sensitizers on mesoporous TiO<sub>2</sub>. The peripheral Ru complexes act as an antenna system by transferring electronic charge to the porphyrin ring. *meso*-Tetrapyrrolylporphyrin coordinated to two Ru complexes converted 21% of the incident photons into current after excitation at the Soret band.

### **Photosensitization of Nanocrystalline SnO<sub>2</sub> Films with a tris(2,2'-Bipyridine) Ruthenium(II)-Fullerene Dyad**

C. NASR, D. M. GULDI, M. MAGGINI, F. PAOLUCCI and S. HOTCHANDANI, *Fullerenes, Nanotubes, Carbon Nanostruct.*, 2003, 11, (2), 121–133

A photoelectrochemical study of a tris(2,2'-bipyridine)ruthenium(II)-C<sub>60</sub> donor-acceptor dyad adsorbed on nanocrystalline semiconductor SnO<sub>2</sub> electrodes was carried out. The results showed that the incident photon-to-current conversion efficiency of the dyad-based photoelectrochemical cells is  $\sim 10\%$ .

## Novel and Efficient Organic Liquid Electrolytes for Dye-Sensitized Solar Cells Based on a Ru(II) Terpyridyl Complex Photosensitizer

K. HARA, T. NISHIKAWA, K. SAYAMA, K. AIKA and H. ARAKAWA, *Chem. Lett.*, 2003, 32, (11), 1014–1015

An electrolyte composed of 1-ethyl-3-methylimidazolium iodide, I<sub>2</sub> and MeCN solvent has been developed for a nanocrystalline TiO<sub>2</sub> solar cell sensitised with a Ru(II) terpyridyl complex (1). Trithiocyanato 4,4',4''-tricarboxy-2,2':6',2''-terpyridine Ru(II) (black dye) was used as (1). Under AM 1.5 irradiation (100 mW cm<sup>-2</sup>), a solar energy-to-electricity conversion efficiency of 8.0% was achieved.

## APPARATUS AND TECHNIQUE

### Thin Film Dissolved Oxygen Sensor Based on Platinum Octaethylporphyrin Encapsulated in an Elastic Fluorinated Polymer

R. N. GILLANDERS, M. C. TEDFORD, P. J. CRILLY and R. T. BAILEY, *Anal. Chim. Acta*, 2004, 502, (1), 1–6

The title sensor (1) was fabricated by encapsulating Pt octaethylporphyrin in an O<sub>2</sub> permeable elastic fluorinated copolymer matrix. Phosphorescence, which was partially quenched by dissolved O<sub>2</sub>, was observed by (1) when (1) was immersed in H<sub>2</sub>O. At elevated temperatures the dye aggregated. (1) exhibits good sensitivity, rapid response and photostability.

### Carbonate-Melt Oxidized Iridium Wire for pH Sensing

M. WANG and S. YAO, *Electroanalysis*, 2003, 15, (20), 1606–1615

A thick, uniform and dense ceramic oxide layer was grown by oxidation on the surface of an Ir wire in molten Li carbonate. After treatment in acid solution, the hydrated oxide layer was characterised as Li<sub>0.86</sub>IrO<sub>2.34</sub>(OH)<sub>0.76</sub>·0.39H<sub>2</sub>O (1). An electrode made with a film of (1) exhibited good pH sensitivity and stability, even in strong acid/base solutions. The electrode has excellent long term stability over 2.5 years.

## HETEROGENEOUS CATALYSIS

### The Influence of Ir and Pt Addition on the Synthesis of Fullerenes at Atmospheric Pressure

G. N. CHURILOV, R. B. WEISMAN, N. V. BULINA, N. G. VNUKOVA, A. P. PUZIR, L. A. SOLOVYOV, S. M. BACHILO, D. A. TSYBOULSKI and G. A. GLUSHENKO, *Fullerenes, Nanotubes, Carbon Nanostruct.*, 2003, 11, (4), 371–382

The addition of metallic Pt and Ir to a fullerene-forming atmospheric-pressure plasma reactor influenced the generation of carbonaceous products. The added metals were efficiently dispersed into the plasma. The addition of Pt increased the proportion of C<sub>60</sub> oxides and decreased the proportion of higher fullerenes, whereas Ir caused a noticeable shift in the fullerene distribution towards C<sub>60</sub>. The Ir also caused a reduction of the soot particle size and the formation of a large quantity of C nanotubes.

### Renewable Hydrogen from Ethanol by Autothermal Reforming

G. A. DELUGA, J. R. SALGE, L. D. SCHMIDT and X. E. VERYKIOS, *Science*, 2004, 303, (5660), 993–997

EtOH and EtOH-H<sub>2</sub>O were found to be converted directly into H<sub>2</sub> with ~ 100% selectivity and > 95% conversion, with a residence time on a Rh/CeO<sub>2</sub> catalyst of < 10 ms. The reactions run at ~ 700°C, but as the process is exothermic, the starting mixture only needs to be heated to ~ 140°C. The mixture is then cooled to 400°C and passed over a Pt/CeO<sub>2</sub> catalyst, where any CO reacts with hot H<sub>2</sub>O to give CO<sub>2</sub> and H<sub>2</sub>. Onboard reforming of liquid fuel into H<sub>2</sub> provides an alternative to storing H<sub>2</sub> for fuel cells.

### Transient Studies of Direct N<sub>2</sub>O Decomposition over Pt–Rh Gauze Catalyst. Mechanistic and Kinetic Aspects of Oxygen Formation

E. V. KONDRATENKO and J. PÉREZ-RAMÍREZ, *Catal. Lett.*, 2003, 91, (3–4), 211–216

Transient experiments were carried out in a temporal analysis of products (TAP) reactor by pulsing N<sub>2</sub><sup>16</sup>O over <sup>18</sup>O-pretreated Pt–Rh gauze catalyst at 1073–1273 K. From isotopic studies and fitting of transient data from N<sub>2</sub>O, N<sub>2</sub> and O<sub>2</sub>, two separate routes for O<sub>2</sub> formation during catalytic N<sub>2</sub>O decomposition were identified. These are: (a) interaction of N<sub>2</sub>O with adsorbed O species formed from N<sub>2</sub>O, and (b) recombination of adsorbed O species on the catalyst surface. The relative contributions of (a) and (b) depend on the reaction temperature.

### Microwave-Assisted Catalytic Transfer Hydrogenation of Safflower Oil

B. L. A. PRABHAVATHI DEVI, M. S. L. KARUNA, K. NARASIMHA RAO, P. S. SAIPRASAD and R. B. N. PRASAD, *JAACS*, 2003, 80, (10), 1003–1005

Catalytic transfer hydrogenation (CTH) of safflower oil using aqueous ammonium formate as H donor and Pd/C as catalyst was carried out in a closed vessel under controlled microwave irradiation conditions. Good selectivity in the complete reduction of linoleic acid to mono-unsaturated acid was achieved with a slight increase in stearic acid, compared to other reported CTH methods. No emulsifier or high ratios of H<sub>2</sub>O to oil were required.

### Improvement of Catalyst Durability by Deposition of Rh on TiO<sub>2</sub> in Photooxidation of Aromatic Compounds

H. EINAGA, T. IBUSUKI and S. FUTAMURA, *Environ. Sci. Technol.*, 2004, 38, (1), 285–289

The deposition of Rh onto TiO<sub>2</sub> improved the TiO<sub>2</sub> catalyst durability in benzene photooxidation. The role of Rh<sup>0</sup> was to reduce the amount of intermediates and byproducts on the catalyst surface. A Rh loading of 0.5–1.0 wt.% produced the highest reaction rate. The deactivation of Rh/TiO<sub>2</sub> was prevented by heat treatment in a flow of H<sub>2</sub> or N<sub>2</sub> after the photoirradiation in humidified air.

## HOMOGENEOUS CATALYSIS

### Process Development and Pilot Plant Scale

#### Synthesis of Spiro[3.5]nonane-6,8-dione

T. E. LEHMANN, O. KUHN and J. KRÜGER, *Org. Process Res. Dev.*, 2003, 7, (6), 913–916

A two step pilot plant process for the production of spiro[3.5]nonane-6,8-dione has been developed. The first step is the epoxidation of spiro[3.5]non-7-en-6-one mediated by sodium perborate. The resulting crude epoxide afforded spiro[3.5]nonane-6,8-dione in 26% overall yield via a Pd-catalysed rearrangement. Pd(PPh<sub>3</sub>)<sub>4</sub> was generated *in situ* from Pd(OAc)<sub>2</sub> and PPh<sub>3</sub> in the presence of triethylamine as the reducing agent. Pd(PPh<sub>3</sub>)<sub>4</sub> formed the active catalytic species upon reaction with *rac*-BINAP.

#### Palladium-Catalyzed Aryl-Amidation. Synthesis of Non-Racemic *N*-Aryl Lactams

R. G. BROWNING, V. BADARINARAYANA, H. MAHMUD and C. J. LOVELY, *Tetrahedron*, 2004, 60, (2), 359–365

The Buchwald-Hartwig aryl amination method was used to obtain a series of chiral, non-racemic *N*-aryl pyrrolidinones from a common pyrrolidinone precursor and the corresponding aryl bromide. The Buchwald catalyst/ligand system was Pd<sub>2</sub>dba<sub>3</sub>/Xantphos. The stereochemical integrity of the *N*-aryl lactam after cross-coupling was proven by synthesis of the racemic compounds and comparison by <sup>1</sup>H NMR spectroscopy using Pirkle's chiral solvating agent.

#### Palladium Catalyzed Reaction in Aqueous DMF: Synthesis of 3-Alkynyl Substituted Flavones in the Presence of Prolinol

M. PAL, V. SUBRAMANIAN, K. PARASURAMAN and K. R. YELESWARAPU, *Tetrahedron*, 2003, 59, (48), 9563–9570

(*S*)-Prolinol facilitated the coupling reaction of terminal alkynes with 3-iodoflavone using (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub> as catalyst and CuI as cocatalyst in aqueous DMF. No significant side reactions such as dimerisation of terminal alkynes or opening of the flavone occur. This is a mild and convenient method for the synthesis of 3-alkynyl substituted flavones of potential biological interest.

#### Cationic Rhodium(I)/PPh<sub>3</sub> Complex-Catalyzed Dehydrogenation of Alkanethiols to Disulfides under Inert Atmosphere

K. TANAKA and K. AJIKI, *Tetrahedron Lett.*, 2004, 45, (1), 25–27

[Rh(cod)]<sub>2</sub>BF<sub>4</sub>/PPh<sub>3</sub> was an effective catalyst system for the dehydrogenation of primary or secondary alkanethiols to symmetrical disulfides under an inert atmosphere of Ar with CH<sub>2</sub>Cl<sub>2</sub> as the solvent. The highest yield of disulfides was achieved at 4°C for 1 h. A longer reaction time (16 h) for the reaction of a primary alkanethiol at the same temperature decreased the yield of disulfides. This dehydrogenation reaction is reversible and the formation of disulfide is a kinetically favourable process.

#### Rhodium Catalysed Coupling Reaction of Myrcene with Ethyl Acetoacetate in the Ionic Liquid 1-Ethyl-3-methylimidazolium Triflimide

K. DHANALAKSHMI and M. VAULTIER, *Tetrahedron*, 2003, 59, (50), 9907–9911

[RhCl(COD)]<sub>2</sub>/TPPMS (triphenylphosphinemonosulfonate sodium salt) can be used for the coupling reaction of myrcene with ethyl acetoacetate in the title ionic liquid [emim][NTf<sub>2</sub>]. The coupling product was obtained in 93% isolated yield without formation of side product. The catalytic system could not be recycled due to its deactivation.

#### Phosphabarrelene-Rhodium Complexes as Highly Active Catalysts for Isomerization Free Hydroformylation of Internal Alkenes

B. BREIT and E. FUCHS, *Chem. Commun.*, 2004, (6), 694–695

Phosphabarrelene-Rh complexes (1) were shown to be extremely active hydroformylation catalysts. Turnover frequencies ≤ 12,000 h<sup>-1</sup> were observed for the hydroformylation of internal cyclic olefins. (1) can enable a position-selective hydroformylation of an internal double bond (C=C) essentially free of alkene isomerisation to occur.

#### Numerical Modeling of Differential Kinetics in the Asymmetric Hydrogenation of Acetophenone by Noyori's Catalyst

R. HARTMANN and P. CHEN, *Adv. Synth. Catal.*, 2003, 345, (12), 1353–1359

An analysis of the catalytic cycle by which *trans*-RuCl<sub>2</sub>[(*S,S*)-binap][(*S,S*)-dppe] asymmetrically hydrogenates acetophenone combines numerical integration of the rate equations and experimental measurement of the time dependence of rates, rather than concentrations. The method yields rate constants for activation, dihydrogen cleavage, and hydride transfer. The turnover-limiting step changes from dihydrogen cleavage to hydride transfer if H<sub>2</sub> pressure is increased, and this also occurs during the acetophenone hydrogenation under typical conditions.

## FUEL CELLS

### The Role of the WO<sub>x</sub> Ad-Component to Pt and PtRu Catalysts in the Electrochemical CH<sub>3</sub>OH Oxidation Reaction

L. X. YANG, C. BOCK, B. MACDOUGALL and J. PARK, *J. Appl. Electrochem.*, 2004, 34, (4), 427–438

High surface area catalysts, Pt/C, PtWO<sub>x</sub>/C, PtRu/C and PtRuWO<sub>x</sub>/C, were prepared via a chemical reduction route using single metal precursor salts. The addition of Ru decreased the particle size. The Ru was found to be partly incorporated into the f.c.c. lattice of Pt and to form a single Ru catalyst component. The PtRuWO<sub>x</sub>/C catalyst has a high degree of catalyst particle agglomeration. Both Ru containing catalysts showed significantly higher activities for the CH<sub>3</sub>OH oxidation reaction.

### Homogeneous and Controllable Pt Particles Deposited on Multi-Wall Carbon Nanotubes as Cathode Catalyst for Direct Methanol Fuel Cells

W. LI, C. LIANG, W. ZHOU, J. QUI, H. LI, G. SUN and Q. XIN, *Carbon*, 2004, 42, (2), 436–439

The size of deposited Pt particles on multi-wall nanotubes (MWNTs) was controlled by using different concentrations of ethylene glycol-deionised (DI) H<sub>2</sub>O. The Pt loading was ~ 10 wt.% for all the samples. The Pt/MWNTs produced using ethylene glycol-5% DI H<sub>2</sub>O exhibit higher O reduction reaction activity and superior cell performance in DMFC tests, than those from 0%, 40% and 70% DI H<sub>2</sub>O.

### Mechanism of Preparation Process and Characterization of Highly Dispersed Pt/C Cathode Electrocatalyst for Direct Methanol Fuel Cells

Z. ZHOU, W. ZHOU, L. JIANG, S. WANG, G. WANG, G. SUN and Q. XIN, *Chin. J. Catal.*, 2004, 25, (1), 65–69

A modified polyol process was used to prepare 40% Pt/C (1) for DMFCs. Highly dispersed Pt nanoparticles with narrow size distribution (mean size of 2.9 nm) supported on C were obtained. DMFC tests indicated that (1) had better electrocatalytic activity and stability for the O reduction reaction in DMFCs than its commercial equivalent. The redox reaction between PtCl<sub>6</sub><sup>2-</sup> and ethylene glycol was confirmed to take place via a single-step reaction path.

### Analysis of the High-Temperature Methanol Oxidation Behaviour at Carbon-Supported Pt–Ru Catalysts

A. S. ARICÒ, V. BAGLIO, A. DI BLASI, E. MODICA, P. L. ANTONUCCI and V. ANTONUCCI, *J. Electroanal. Chem.*, 2003, 557, 167–176

MeOH oxidation (1) at three Pt–Ru catalysts varying by the concentration of active phase on the C support was investigated at 80–130°C. When the catalyst had intrinsically high catalytic activity the fuel cell performance was enhanced, but the MeOH reaction rate was less influenced by an increase in coverage of active species. Catalysts with a higher degree of alloying and metallic behaviour on the surface are more active towards (1).

### Preparation of Pt–Ru Bimetallic Anodes by Galvanostatic Pulse Electrodeposition: Characterization and Application to the Direct Methanol Fuel Cell

C. COUTANCEAU, A. F. RAKOTONDRAINIBÉ, A. LIMA, E. GARNIER, S. PRONIER, J.-M. LÉGER and C. LAMY, *J. Appl. Electrochem.*, 2004, 34, (1), 61–66

Using a galvanostatic pulse electrodeposition technique, Pt and Ru were electrodeposited on C electrodes to prepare DMFC anodes (1) with different Pt:Ru atomic ratios. Most of (1) consisted of 2 mg cm<sup>-2</sup> of Pt–Ru alloy particles with the desired composition and with particle sizes of 5–8 nm. Electrochemical tests in a single DMFC found that the best Pt:Ru atomic ratio at 50–110°C was 80:20.

### Carbon-Supported Pt–Fe Alloy as a Methanol-Resistant Oxygen-Reduction Catalyst for Direct Methanol Fuel Cells

A. K. SHUKLA, R. K. RAMAN, N. A. CHOUDHURY, K. R. PRIOLKAR, P. R. SARODE, S. EMURA and R. KUMASHIRO, *J. Electroanal. Chem.*, 2004, 563, (2), 181–190

The electrocatalyst Pt–Fe/C crystallises in an ordered f.c.t. crystal structure with higher proportions of active Pt sites than Pt/C. Pt–Fe/C exhibits significantly high O reduction activity in the presence of MeOH, while Pt/C shows a MeOH poisoning effect under similar conditions.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Molecule-Independent Electrical Switching in Pt/Organic Monolayer/Ti Devices

D. R. STEWART, D. A. A. OHLBERG, P. A. BECK, Y. CHEN, R. STANLEY WILLIAMS, J. O. JEPPESEN, K. A. NIELSEN and J. FRASER STODDART, *Nano Lett.*, 2004, 4, (1), 133–136

Electronic devices (1) comprising a Langmuir–Blodgett molecular layer sandwiched between planar Pt and Ti metal electrodes were shown to function as switches and tunable resistors over a 10<sup>2</sup>–10<sup>5</sup> Ω range under current or voltage control. Reversible hysteretic switching and resistance tuning was qualitatively similar for the very different molecular species: Cd eicosanoate salt, an amphiphilic [2]rotaxane (R) and the dumbbell-only component of R.

### Structural and Morphological Characterization by Energy Dispersive X-ray Diffractometry and Reflectometry Measurements of Cr/Pt Bilayer Films

B. PACI, A. GENEROSI, V. R. ALBERTINI, E. AGOSTINELLI, G. VARVARO and D. FIORANI, *Chem. Mater.*, 2004, 16, (2), 292–298

Double-layer Cr/Pt thin films were deposited by pulsed laser deposition at room temperature to 600°C, both on crystalline (Si and MgO) and on amorphous (SiO<sub>2</sub>) substrates. Epitaxial films with a very good texture and a very smooth surface were obtained. With the excimer laser at an energy fluence of 5 J cm<sup>-2</sup>, the Pt/Cr multilayer shows a high crystalline quality independent of deposition temperature.

### Ballistic Transport in Metallic Nanotubes with Reliable Pd Ohmic Contacts

D. MANN, A. JAVEY, J. KONG, Q. WANG and H. DAI, *Nano Lett.*, 2003, 3, (11), 1541–1544

Contacting metallic single-walled C nanotubes by Pd gave highly reproducible ohmic contacts, which were used for an examination of ballistic transport in metallic nanotubes. The Pd ohmic contacts were more reliable than previously used Ti ohmic contacts. Pt gave non-ohmic contacts to metallic nanotubes. The length of the nanotube under the metal contact area is electrically turned off; transport occurs from metal to nanotube at the edge of the contacts.