

# Abstracts

## CATALYSIS – APPLIED AND PHYSICAL ASPECTS

### Continuous Flow Hydrogenation Using Polysilane-Supported Palladium/Alumina Hybrid Catalysts

H. Oyamada, T. Naito and S. Kobayashi, *Beilstein J. Org. Chem.*, 2011, **7**, 735–739

Continuous flow systems for hydrogenation using Pd/(PSi–Al<sub>2</sub>O<sub>3</sub>) (PSi = polysilane) hybrid catalysts were developed. The original Pd/(PSi–Al<sub>2</sub>O<sub>3</sub>) catalysts were used in these systems for the hydrogenation of unsaturated C–C bonds and a nitro group, deprotection of a carbobenzyloxy group, and a dehalogenation reaction. High catalytic activity was retained for at least 8 h under neat conditions. No Pd leaching was detected. The hydrogenation reactions could also be carried out successfully in water.

## CATALYSIS – REACTIONS

### Direct Synthesis of Hydrogen Peroxide from Hydrogen and Oxygen over a Pd Core-Silica Shell Catalyst

H.-J. Lee, S. Kim, D.-W. Lee and K.-Y. Lee, *Catal. Commun.*, 2011, **12**, (11), 968–971

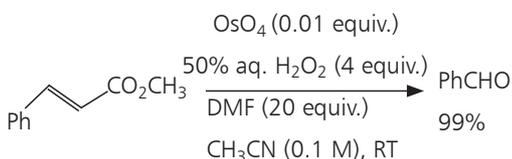
Pd core-silica shell particles (Pd@SiO<sub>2</sub>) were obtained by encapsulating Pd colloidal NPs with a SiO<sub>2</sub> shell *via* the Stöber method. The Pd core NPs were well dispersed and had uniform size (4 nm) and shape inside the porous SiO<sub>2</sub> shell. Pd@SiO<sub>2</sub> showed high performance for the direct synthesis of H<sub>2</sub>O<sub>2</sub>, which was better than those of impregnated Pd/SiO<sub>2</sub> and Pd/Al<sub>2</sub>O<sub>3</sub>.

### Catalytic Oxidative Cleavage of Olefins Promoted by Osmium Tetroxide and Hydrogen Peroxide

S. R. Hart, D. C. Whitehead, B. R. Travis and B. Borhan, *Org. Biomol. Chem.*, 2011, **9**, (13), 4741–4744

H<sub>2</sub>O<sub>2</sub> was employed as the terminal oxidant in the OsO<sub>4</sub>-mediated oxidative cleavage of olefins, producing aldehyde and ketone products. Aryl olefins were cleaved in good to excellent yield. Alkyl olefins cleaved in moderate to good yield for di- and tri-substituted alkenes. The use of the more environmentally benign H<sub>2</sub>O<sub>2</sub> as the terminal oxidant *in lieu* of Oxone addresses concerns about the salt stream associated with the original protocol.

S. R. Hart *et al.*, *Org. Biomol. Chem.*, 2011, **9**, (13), 4741–4744



## EMISSIONS CONTROL

### A Review of NO<sub>x</sub> Storage/Reduction Catalysts: Mechanism, Materials and Degradation Studies

G. Liu and P.-X. Gao, *Catal. Sci. Technol.*, 2011, **1**, (4), 552–568

NSR is employed for lean-burn gasoline and diesel vehicles. This Minireview covers reaction mechanisms, degradation mechanisms and catalyst developments. The NSR reaction and degradation mechanisms are discussed based on a typical NSR catalyst Pt/BaO/Al<sub>2</sub>O<sub>3</sub>, along with NSR catalyst developments for enhancing performance and alleviating their S poisoning and thermal degradation. (Contains 137 references.)

### Modeling the Effects of Pt Loading on NO<sub>x</sub> Storage on Pt/BaO/Al<sub>2</sub>O<sub>3</sub> Catalysts

J. Xu, M. P. Harold and V. Balakotaiah, *Appl. Catal. B: Environ.*, 2011, **104**, (3–4), 305–315

A microkinetic model was developed for NO<sub>x</sub> storage on a series of Pt/BaO/Al<sub>2</sub>O<sub>3</sub> catalysts with Pt loadings from 0–3.7 wt%. Ba sites were classified into two storage site populations: proximal and non-proximal (bulk). A simple model for estimating the capacities of the two Ba site populations using the Pt loading was used to explain trends in the storage of NO/O<sub>2</sub> and NO<sub>2</sub>/O<sub>2</sub> and integrates existing literature models for NO<sub>2</sub> storage on BaO/Al<sub>2</sub>O<sub>3</sub>, Pt-catalysed NO oxidation to NO<sub>2</sub>, and spillover chemistry involving NO<sub>2</sub>. The model shows reasonable agreement with the measured storage of NO and NO<sub>2</sub> in O<sub>2</sub> at 340°C for a range of storage times and Pt loadings.

## FUEL CELLS

### Platinum Catalyst Degradation in Phosphoric Acid Fuel Cells for Stationary Applications

T. T. Aindow, A. T. Haug and D. Jayne, *J. Power Sources*, 2011, **196**, (10), 4506–4514

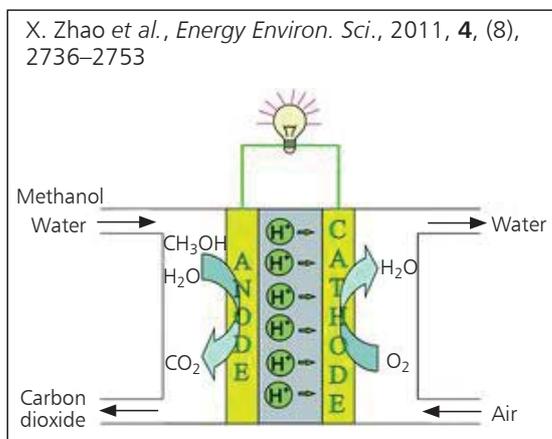
The fundamental decay mechanism of Pt alloy cathode

catalysts for PAFCs was studied with a surface area loss model and experimental electrochemical surface area measurements after real-world operation. The rate of change in electrochemical surface area was found to be affected by both time and temperature. The results suggest that Pt particle migration and coalescence on the C support surface is the dominant mechanism for surface area change in these PAFC catalysts.

### Recent Advances in Catalysts for Direct Methanol Fuel Cells

X. Zhao, M. Yin, L. Ma, L. Liang, C. Liu, J. Liao, T. Lu and W. Xing, *Energy Environ. Sci.*, 2011, **4**, (8), 2736–2753

This Perspective reviews potential pathways for increasing the cost-effectiveness and efficiency of low Pt alloys and core-shell-like catalysts, Pd-Me (Me = Co, Fe, etc.), Ru-Se and heat-treated  $\text{MeN}_x\text{C}_y$ -based catalysts for DMFCs (see the **Figure**). Fundamental understanding of the composition–activity and structure–activity relationships, innovative synthesis and promising development directions are highlighted. The main degradation mechanism of the catalysts and the corresponding mitigating strategies are presented. (Contains 262 references.)



Reproduced by permission of The Royal Society of Chemistry

### Platinum Monolayer on IrFe Core–Shell Nanoparticle Electrocatalysts for the Oxygen Reduction Reaction

K. Sasaki, K. A. Kuttiyiel, D. Su and R. R. Adzic, *Electrocatalysis*, 2011, **2**, (2), 134–140

Highly active and stable Pt monolayer on C-supported IrFe core-shell NP ( $\text{Pt}_{\text{ML}}/\text{IrFe}/\text{C}$ ) electrocatalysts were synthesised. IrFe core-shell NPs were prepared by chemical reduction and subsequent thermal

annealing. Pt monolayers were deposited on the IrFe core-shell NPs by galvanic replacement of underpotentially deposited Cu adatoms on the Ir shell surfaces. The specific and Pt mass activities for the ORR on the  $\text{Pt}_{\text{ML}}/\text{IrFe}/\text{C}$  electrocatalyst were  $0.46 \text{ mA cm}^{-2}$  and  $1.1 \text{ A mg}_{\text{Pt}}^{-1}$ , respectively. The catalysts were shown to have high durability.

### The Study on the Dynamic Response Performance of PEMFC with Electrodeposited $\text{RuO}_2 \cdot x\text{H}_2\text{O}-\text{Pt}/\text{C}$ Electrode

Y. Wu, X. Wu, H. Xu and L. Lu, *J. Nat. Gas Chem.*, 2011, **20**, (3), 256–260

Electrodeposited  $\text{RuO}_2 \cdot x\text{H}_2\text{O}-\text{Pt}/\text{C}$  was characterised by SEM-EDS, which confirmed that  $\text{RuO}_2 \cdot x\text{H}_2\text{O}$  was electrodeposited on the surface of Pt/C. The performance of single cells with and without  $\text{RuO}_2 \cdot x\text{H}_2\text{O}-\text{Pt}/\text{C}$  at the cathode was studied using CV, electrochemical impedance spectra and polarisation curve techniques. When the PEMFC modified with  $\text{RuO}_2 \cdot x\text{H}_2\text{O}-\text{Pt}/\text{C}$  was operated at lower pressure, a faster and more stable dynamic response was found. Modifying with  $\text{RuO}_2 \cdot x\text{H}_2\text{O}-\text{Pt}/\text{C}$  not only slightly increases the single cell performance but also dramatically improves the dynamic response performance.

## METALLURGY AND MATERIALS

### Gold-Platinum Nanoparticles: Alloying and Phase Segregation

B. N. Wanjala, J. Luo, B. Fang, D. Mott and C.-J. Zhong, *J. Mater. Chem.*, 2011, **21**, (12), 4012–4020

The phase and surface properties of supported AuPt NPs have been shown to range from single-phase alloy, partial alloy, to phase-segregated structures depending on the preparation conditions, bimetallic composition and supporting materials. This conclusion was also supported by DFT computation for small AuPt clusters and molecular dynamics simulations for AuPt NPs of various sizes. For AuPt NPs supported on C materials, the nanoscale alloying or phase segregation was demonstrated to be controllable by thermal treatment temperatures.

## APPARATUS AND TECHNIQUE

### Novel PdAgCu Ternary Alloy: Hydrogen Permeation and Surface Properties

A. M. Tarditi, F. Braun and L. M. Cornaglia, *Appl. Surf. Sci.*, 2011, **257**, (15), 6626–6635

Dense PdAgCu composite membranes were prepared by the sequential electroless plating of Pd, Ag and Cu on top of both disk and tubular porous stainless steel substrates. The H<sub>2</sub> permeation performance was investigated over 350–450°C and a trans-membrane pressure up to 100 kPa. After annealing at 500°C in a H<sub>2</sub> stream followed by permeation experiments, the alloy layer had a fcc crystalline phase with a bulk concentration (by EDS) of: 68% Pd; 7% Ag; and 25% Cu. The PdAgCu tubular membrane was stable for more than 300 h in a H<sub>2</sub> stream. The permeabilities of the PdAgCu samples were higher than the permeabilities of PdCu membranes with a fcc phase. The cosegregation of Ag and Cu to the membrane surface was observed after H<sub>2</sub> permeation experiments at high temperature.

## ELECTRICAL AND ELECTRONICS

### Characterization of IrO<sub>2</sub>/CNT Nanocomposites

Y. M. Chen, Y. S. Huang, K. Y. Lee, D. S. Tsai and K. K. Tiong, *J. Mater. Sci.: Mater. Electron.*, 2011, **22**, (7), 890–894

IrO<sub>2</sub> nanocrystals (NCs) were grown on vertically aligned CNT templates, forming IrO<sub>2</sub>/CNT nanocomposites, by MOCVD using (C<sub>6</sub>H<sub>7</sub>)(C<sub>8</sub>H<sub>12</sub>)Ir. The nanocomposites were characterised using FESEM, TEM, XRD and Raman scattering. The IrO<sub>2</sub> varied from particle- to tube-like NCs as the deposition time increased (5–60 min). The particle-like IrO<sub>2</sub> NCs may be used as a protective layer on CNTs, providing stable and uniform FE properties. The tube-like structure may increase the surface-to-volume ratio which makes the IrO<sub>2</sub>/CNT nanocomposites possible candidates for supercapacitor applications.

## MEDICAL AND DENTAL

### Conjugated Polyelectrolyte–Cisplatin Complex Nanoparticles for Simultaneous *in Vivo* Imaging and Drug Tracking

D. Ding, K. Li, Z. Zhu, K.-Y. Pu, Y. Hu, X. Jiang and B. Liu, *Nanoscale*, 2011, **3**, (5), 1997–2002

A molecular brush based on a conjugated polyelectrolyte (CPE) grafted with dense PEG chains was complexed with cisplatin to form cisplatin-loaded NPs (CPE–PEG–Pt). The obtained NPs have high far-red/near-infrared fluorescence and are able to release the drug in a continuous and slow manner. These NPs were used to visualise HepG2 cancer cells. The NPs also served as an *in vivo* fluorescent imaging probe that simultaneously tracks the *in vivo* drug distribution in mice upon intravenous administration.

### Rationally Engineered Polymeric Cisplatin Nanoparticles for Improved Antitumor Efficacy

A. Paraskar, S. Soni, S. Basu, C. J. Amarasiriwardena, N. Lupoli, S. Srivats, R. Sinha Roy and S. Sengupta, *Nanotechnology*, 2011, **22**, (26), 265101

A novel PEG-functionalised poly-isobutylene-maleic acid (PEG–PIMA) copolymer, which can complex with *cis*-Pt(II) through a monocarboxylato and a coordinate bond has been used to engineer a novel NP. This complex self-assembles into a PEG–PIMA–cisplatin NP and exhibits an IC<sub>50</sub> = 0.77 ± 0.11 μM, comparable to that of free cisplatin (IC<sub>50</sub> = 0.44 ± 0.09 μM). The NPs are internalised into the endolysosomal compartment of cancer cells, and release cisplatin in a pH-dependent manner.

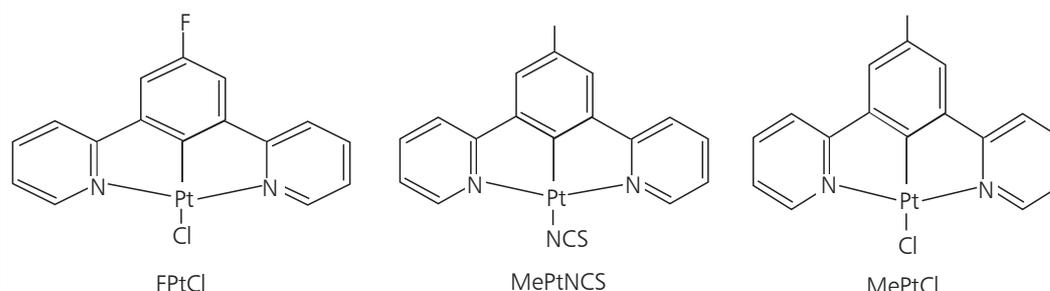
## PHOTOCONVERSION

### Cyclometallated Platinum(II) Complexes of 1,3-Di(2-pyridyl)benzenes for Solution-Processable WOLEDs Exploiting Monomer and Excimer Phosphorescence

W. Mróz, C. Botta, U. Giovannella, E. Rossi, A. Colombo, C. Dragonetti, D. Roberto, R. Ugo, A. Valore and J. A. G. Williams, *J. Mater. Chem.*, 2011, **21**, (24), 8653–8661

N<sup>^</sup>C<sup>^</sup>N-5-Fluoro-1,3-di(2-pyridyl)benzene platinum(II)

W. Mróz et al., *J. Mater. Chem.*, 2011, **21**, (24), 8653–8661



chloride, "FPtCl", and N<sup>5</sup>-methyl-1,3-di(2-pyridyl)-benzene platinum(II) isothiocyanate, "MePtNCS", were synthesised and then characterised. Both were found to be highly efficient phosphorescent green emitters and could also display excimer emission in the red region. They were studied as triplet emitters in solution-processed, multilayer OLEDs, and compared to the known complex of 5-methyl-1,3-di(2-pyridyl)-benzene, "MePtCl". "FPtCl" was the most efficiently emitting complex and was used as the dopant in a solution-processed WOLED.

#### **New Design Tactics in OLEDs Using Functionalized 2-Phenylpyridine-Type Cyclometalates of Iridium(III) and Platinum(II)**

G. Zhou, W.-Y. Wong and X. Yang, *Chem. Asian J.*, 2011, **6**, (7), 1706–1727

This Focus Review highlights recent design tactics to develop functional metallophosphors for future OLED devices. Functionalised phosphorescent Ir(III) and Pt(II) ppy-type cyclometallated complexes show better prospects than their unfunctionalised counterparts in terms of switchable emission wavelength, phosphorescent quantum yield and phosphorescent lifetime. The aims are to enhance device efficiency and suppress efficiency roll-off, to achieve versatile colour tuning and simple device manufacture, and to obtain high quality white light from WOLEDs. (Contains 39 references.)