

# ABSTRACTS

## CATALYSIS – APPLIED AND PHYSICAL ASPECTS

### Hydrogenation of Natural Rubber Latex in the Presence of [Ir(cod)(PCy<sub>3</sub>)(py)]PF<sub>6</sub>

A. MAHITTIKUL, P. PRASASSARAKICH and G. L. REMPEL, *J. Mol. Catal. A: Chem.*, 2009, 297, (2), 135–141

[Ir(COD)(PCy<sub>3</sub>)(py)]PF<sub>6</sub> (1) was an effective catalyst for the hydrogenation of natural rubber latex (NRL) in monochlorobenzene. The hydrogenation was first-order with respect to both H<sub>2</sub> pressure and concentration of (1), which suggests that the active complex is mononuclear. Addition of a sulfonic acid helped suppress the poisoning of (1) by impurities in the NRL.

## CATALYSIS – REACTIONS

### Pd Nanoparticles Immobilized on Sepiolite by Ionic Liquids: Efficient Catalysts for Hydrogenation of Alkenes and Heck Reactions

R. TAO, S. MIAO, Z. LIU, Y. XIE, B. HAN, G. AN and K. DING, *Green Chem.*, 2009, 11, (1), 96–101

Pd/sepiolite catalysts (1) were prepared by immobilising Pd<sup>2+</sup> on sepiolite using an ionic liquid containing a guanidine cation, followed by reduction with H<sub>2</sub> at 150°C. XPS established that the loaded Pd is mainly Pd(0), with a small amount of its oxides, and distributed uniformly with particle size ~ 5 nm, as confirmed by TEM. (1) exhibited very high efficiency for the hydrogenation of alkenes and Heck reactions.

### Catalyst Leaching as an Efficient Tool for Constructing New Catalytic Reactions: Application to the Synthesis of Cyclic Vinyl Sulfides and Vinyl Selenides

V. P. ANANIKOV, K. A. GAYDUK, I. P. BELETSKAYA, V. N. KHRUSTALEV and M. YU. ANTIPIN, *Eur. J. Inorg. Chem.*, 2009, (9), 1149–1161

Catalyst leaching from Pd and Ni particles stabilised by organic S and Se ligands was found to occur in solution in the presence of phosphanes. This process was monitored in real time by 1D and 2D NMR. The metal particle leaching was used to generate a new catalytic system for the synthesis of the title compounds from alkynes and dichalcogenides.

## EMISSIONS CONTROL

### The Effect of Sulphur on the Activity of Pd/Al<sub>2</sub>O<sub>3</sub>, Pd/CeO<sub>2</sub> and Pd/ZrO<sub>2</sub> Diesel Exhaust Gas Catalysts

T. KOLLI, M. HUUHTANEN, A. HALLIKAINEN, K. KALLINEN and R. L. KEISKI, *Catal. Lett.*, 2009, 127, (1–2), 49–54

Pd/Al<sub>2</sub>O<sub>3</sub>, Pd/CeO<sub>2</sub> and Pd/ZrO<sub>2</sub> diesel oxidation catalysts and their washcoat materials were studied after S treatment. The catalytic activities were analysed in a simplified diesel exhaust gas mixture by FTIR spectroscopy. S treatment was shown to deactivate these Pd-based diesel oxidation catalysts.

### Cleaner Water Using Bimetallic Nanoparticle Catalysts

M. S. WONG, P. J. J. ALVAREZ, Y.-L. FANG, N. AKÇIN, M. O. NUTT, J. T. MILLER and K. N. HECK, *J. Chem. Technol. Biotechnol.*, 2009, 84, (2), 158–166

Pd-based catalysts are effective in hydrodechlorination of chlorinated ethenes and related compounds. However Pd-on-Au bimetallic nanoparticles (1) were recently found to exhibit superior catalytic activity and improved deactivation resistance for groundwater remediation. (1) are significant in the development of a viable hydrodechlorination catalysis technology.

## FUEL CELLS

### Mechanism Study of the Ethanol Oxidation Reaction on Palladium in Alkaline Media

Z. X. LIANG, T. S. ZHAO, J. B. XU and L. D. ZHU, *Electrochim. Acta*, 2009, 54, (8), 2203–2208

The mechanism of the EtOH oxidation reaction (EOR) on a Pd electrode (1) in alkaline media was studied using CV. The dissociative adsorption of EtOH proceeded quickly and the rate-determining step was the removal of the adsorbed ethoxide ion by the adsorbed hydroxyl ion on (1). At potentials below –0.4 V, the Tafel slope was 130 mV dec<sup>-1</sup>. At potentials above –0.4 V, the Tafel slope increased to 250 mV dec<sup>-1</sup>, as the mechanism of the EOR was complicated by oxide layer formation on the Pd surface at higher potentials.

## METALLURGY AND MATERIALS

### Growth and Field Emission of Reactive Sputtered Pd–PdO Core–Shell Nanoflakes on Platinum

C.-J. HUANG, F.-M. PAN, T.-C. TZENG, L. CHANG and J.-T. SHEU, *J. Electrochem. Soc.*, 2009, 156, (2), J28–J31

PdO was reactive sputter deposited on Pt. The PdO thin film grown had a flakelike morphology. The nanosized flake had a core–shell structure with a single Pd grain encapsulated by a crystalline PdO surface layer. The formation of the nanoflakes is attributed to a large interfacial stress due to a lattice mismatch between PdO and Pt.

### High Temperature Interface Reactions of TiC, TiN, and SiC with Palladium and Rhodium

P. DEMKOWICZ, K. WRIGHT, J. GAN and D. PETTI, *Solid State Ionics*, 2008, 179, (39), 2313–2321

Reactions of TiC, TiN and SiC with Pd and Rh at ≤ 1600°C were studied using bulk diffusion couple experiments. Intermetallic phases at the ceramic–metal interfaces were observed. The reactivity order of the ceramics was: SiC >> TiC > TiN, and reactivity order of the pgms was: Pd > Rh. The TiN–Pd interfaces gave no intermetallic phase formation under the annealing conditions. The formation of distinct intermetallic phases at the SiC–Rh and TiC–Rh interfaces followed a non-parabolic behaviour.

## Synthesis and Structure-Specific Functions of Patchy Nanoparticles

T. TERANISHI, M. SARUYAMA and M. KANEHARA, *Chem. Lett.*, 2009, 38, (3), 194–199

The close coupling of different components on the nanoscale in anisotropically phase-segregated nanoparticles, 'patchy nanoparticles', may improve performance for various applications or even create new properties. A seed-mediated growth method was used to synthesise patchy nanoparticles consisting of a combination of metals, metal sulfides and metal oxides, such as PdS<sub>x</sub>/Co<sub>9</sub>S<sub>8</sub> and CdS/Pd<sub>x</sub>Cd<sub>y</sub>S/CdS.

## CHEMISTRY

### Kinetics of Complex Formation between Palladium(II) Acetate and Bis(diphenylphosphino)ferrocene

M. POURSHAHBAZ, M. IRANDOUST, E. RAFIEE and M. JOSHAGHANI, *Polyhedron*, 2009, 28, (3), 609–613

<sup>31</sup>P NMR spectroscopy was used to study the kinetics of complex formation between Pd(OAc)<sub>2</sub> and dppf. The mole ratio and the <sup>31</sup>P-chemical shifts in DMSO-*d*<sub>6</sub> revealed the formation of an intermediate, which gradually converts into the more stable [Pd(dppf)(OAc)<sub>2</sub>] with dppf acting as a chelate ligand. In CDCl<sub>3</sub>, [Pd(dppf)(OAc)<sub>2</sub>] was formed directly. The rate constant for the complexation was evaluated.

### Photophysical Properties, X-Ray Structures, Electrochemistry, and DFT Computational Chemistry of Osmium Complexes

B. CARLSON, B. E. EICHINGER, W. KAMINSKY, J. P. BULLOCK and G. D. PHELAN, *Inorg. Chim. Acta*, 2009, 362, (5), 1611–1618

Phosphorescent [Os(N–N)<sub>2</sub>(L–L) or Os(L–L)<sub>2</sub>(N–N)]<sup>2+</sup> (PF<sub>6</sub>)<sub>2</sub> (N–N = derivative of 1,10-phenanthroline; L–L = 1,2-bis(dimethylphosphino)ethane, 1,2-bis(dicyclohexylphosphino)ethane or 1,2-bis(dimethylarseno)benzene) were synthesised. The luminescence emission lifetimes of Os(II)(L–L)<sub>2</sub>(N–N) were longer than those of Os(II)(N–N)<sub>2</sub>(L–L). DFT calculations show that there is significant mixing of the π–π\* into the dπ–π\* charge-transfer state for Os(II)(L–L)<sub>2</sub>(N–N) giving a longer lived excited state.

## ELECTRICAL AND ELECTRONICS

### Direct-Write Patterning Palladium Colloids as a Catalyst for Electroless Metallization for Microwave Composites

D. ZABETAKIS, P. LOSCHIALPO, D. SMITH, M. A. DINDERMAN and W. J. DRESSICK, *Langmuir*, 2009, 25, (3), 1785–1789

Inkjet printing was used to pattern a Pd–Sn electroless catalyst (Cataposit 44, Rohm & Haas) for electroless Cu metallisation on paper. Low-resistance Cu tracings can be produced. Large-area microscale patterning was demonstrated. Sample patterns of frequency-selective surface designs were manufactured and shown to conform to computationally modelled expectations in the microwave regime.

### Effect of pH in Ru Slurry with Sodium Periodate on Ru CMP

I.-K. KIM, B.-G. CHO, J.-G. PARK, J.-Y. PARK and H.-S. PARK, *J. Electrochem. Soc.*, 2009, 156, (3), H188–H192

NaIO<sub>4</sub> acted as both oxidant and etchant on a Ru chemical mechanical planarisation slurry for the formation of Ru bottom electrodes in DRAM capacitors. Below pH 7.5, a high static etch rate was measured due to dissolution of RuO<sub>4</sub>. Above pH 7.5, the static etch rate decreased due to formation of insoluble RuO<sub>2</sub>·2H<sub>2</sub>O and depletion of periodate ions. A Ru to oxide selectivity of ~ 23:1 was achieved at pH 8–9. In a slurry of pH 9, Ru overetching was prevented.

## ELECTROCHEMISTRY

### Electrochemical Preparation of Pd Nanorods with High-Index Facets

N. TIAN, Z.-Y. ZHOU and S.-G. SUN, *Chem. Commun.*, 2009, (12), 1502–1504

Fivefold twinned Pd nanorods (1) with {*bkk*} or {*bk0*} high-index facets were obtained using an electrochemical square-wave potential method with well-controlled potential limits. This is attributed to the different degrees of surface reconstruction induced by O<sub>2</sub> adsorption/desorption. (1) with {*bkk*} high-index facets exhibited 2–3 times higher catalytic activity per unit surface area than a commercial Pd black catalyst towards the electrooxidation of EtOH in alkaline solution (0.1 M NaOH + 0.1 M EtOH).

## PHOTOCONVERSION

### New NIR-Emitting Complexes of Platinum(II) and Palladium(II) with Fluorinated Benzoporphyrins

S. M. BORISOV, G. NUSS, W. HAAS, R. SAF, M. SCHMUCK and I. KLIMANT, *J. Photochem. Photobiol. A: Chem.*, 2009, 201, (2–3), 128–135

Pt(II) and Pd(II) complexes with fluorinated benzoporphyrins were synthesised. The complexes possess highly efficient room temperature Near IR phosphorescence and are excitable with blue and red light. The fluorinated derivatives exhibited improved photophysical properties and photostability. The new dyes can be used as indicators in optical O<sub>2</sub> sensors.

### Luminescence Color Change of a Platinum(II) Complex Solid Upon Mechanical Grinding

T. ABE, T. ITAKURA, N. IKEDA and K. SHINOZAKI, *Dalton Trans.*, 2009, (4), 711–715

The yellow luminescence of crystalline Pt(5dpb)Cl (5dpbH = 1,3-di(5-methyl-2-pyridyl)benzene) changed to orange when grinding into fine powder on a glass substrate. A broad emission band was observed at ~ 670 nm for the powder. This disappeared below 120 K. Pt(dpb)Cl (dpbH = 1,3-di(2-pyridyl)benzene) also exhibited luminescent mechanochromism. However, the broad emission that appeared upon grinding still remained at 77 K; the ground sample of Pt(dpb)Cl was amorphous.