

# ABSTRACTS

## CATALYSIS – APPLIED AND PHYSICAL ASPECTS

### Catalytically Active, Magnetically Separable, and Water-Soluble FePt Nanoparticles Modified with Cyclodextrin for Aqueous Hydrogenation Reactions

K. MORI, N. YOSHIOKA, Y. KONDO, T. TAKEUCHI and H. YAMASHITA, *Green Chem.*, 2009, 11, (9), 1337–1342

Thermal decomposition of  $\text{Fe}(\text{CO})_5$ , followed by reduction of  $\text{Pt}(\text{acac})_2$  in the presence of oleic acid and oleylamine, gave FePt nanoparticles (1) with Fe-rich cores and Pt-rich shells. (1) were subsequently treated with  $\gamma$ -cyclodextrin ( $\gamma$ -CD). FePt- $\gamma$ -CD (2) exhibited superparamagnetic behaviour at 300 K. (2) was used for aqueous hydrogenation reactions, with easy recovery of (2) by applying an external magnet.

### Catalytic Inactivation of Bacteria Using Pd-Modified Titania

L. R. QUISENBERRY, L. H. LOETSCHER and J. E. BOYD, *Catal. Commun.*, 2009, 10, (10), 1417–1422

For the photocatalytic sterilisation of *Escherichia coli* in  $\text{H}_2\text{O}$ , Pd/TiO<sub>2</sub> was faster than Pt/TiO<sub>2</sub>. Pd/TiO<sub>2</sub> was also active in the absence of light. Pd/TiO<sub>2</sub> temporarily lost bactericidal activity after use, but was reactivated in air. It is proposed that the Pd metal on the surface of Pd/TiO<sub>2</sub> is reduced in solution during the reaction, and must be reoxidised to regain activity. The reduction may initiate the bactericidal activity.

## CATALYSIS – REACTIONS

### Iridium Catalysed Alkylation of 4-Hydroxy Coumarin, 4-Hydroxy-2-quinolones and Quinolin-4(1H)-one with Alcohols under Solvent Free Thermal Conditions

R. GRIGG, S. WHITNEY, V. SRIDHARAN, A. KEEP and A. DERRICK, *Tetrahedron*, 2009, 65, (36), 7468–7473

Ir-catalysed alkylation of the title compounds with substituted benzyl and aliphatic alcohols under solvent-free heating gave the monoalkylated products in high to excellent yield. 3,3'-Bis (heterocyclyl) methane products can arise *via* a Michael addition pathway. The alkylation of 4-hydroxy-1-methyl-2(1H)-quinoline with BzOH, KOH and the Ir chloro-bridged  $[\text{Cp}^*\text{IrCl}_2]_2$  dimer was carried out at 110°C for 48 h in a sealed tube.

### An Alternative Synthesis of Tamiflu®: A Synthetic Challenge and the Identification of a Ruthenium-Catalyzed Dihydroxylation Route

K. YAMATSUGU, M. KANAI and M. SHIBASAKI, *Tetrahedron*, 2009, 65, (31), 6017–6024

A Ru-catalyzed dihydroxylation synthetic route was identified for Tamiflu®, which removes the need for a Mitsunobu inversion step. Only 0.5 mol% of RuCl<sub>3</sub> was required. The use of explosive trifluoroacetic acid, generated *in situ*, is also avoided.

## EMISSIONS CONTROL

### Re-evaluation and Modeling of a Commercial Diesel Oxidation Catalyst

Y.-D. KIM and W.-S. KIM, *Ind. Eng. Chem. Res.*, 2009, 48, (14), 6579–6590

A modelling approach to predict the performance of a DOC used published experimental data and a new set of conversion experiments. Steady-state experiments with DOCs (Pt supported on an Al<sub>2</sub>O<sub>3</sub> washcoat) mounted on a light-duty turbocharged diesel engine were carried out. The reaction rates for CO, HC, and NO oxidations in diesel exhaust over fresh Pt/Al<sub>2</sub>O<sub>3</sub> were determined in conjunction with a transient 1D heterogeneous plug-flow reactor model.

### NOx Abatement for Lean-Burn Engines under Lean-Rich Atmosphere over Mixed NSR-SCR Catalysts: Influences of the Addition of a SCR Catalyst and of the Operational Conditions

E. C. CORBOS, M. HANEDA, X. COURTOIS, P. MARECOT, D. DUPREZ and H. HAMADA, *Appl. Catal. A: Gen.*, 2009, 365, (2), 187–193

The NO<sub>x</sub> removal efficiency of a Pt-Rh/Ba/Al<sub>2</sub>O<sub>3</sub> NSR model catalyst under a lean/rich atmosphere was improved by the addition of a SCR catalyst (Co/Al<sub>2</sub>O<sub>3</sub> or Cu/ZSM-5). Both SCR catalysts were able to reduce NO<sub>x</sub> using the NH<sub>3</sub> formed during the rich cycles on Pt-Rh/Ba/Al<sub>2</sub>O<sub>3</sub>. With Cu/ZSM-5, this was independent of the reductant used (CO or H<sub>2</sub>) and of the reduction time (10, 5 or 2.5 s).

## FUEL CELLS

### Origin and Quantitative Analysis of the Constant Phase Element of a Platinum SOFC Cathode Using the State-Space Model

S. RICCIARDI, J. C. RUIZ-MORALES and P. NUÑEZ, *Solid State Ionics*, 2009, 180, (17–19), 1083–1090

A SOFC cathode was investigated using SEM, electrochemical impedance spectroscopy and simulations using the state-space model. The kinetic parameters were determined. The triple phase boundary length was measured and its width deduced. A quantitative analysis of the constant phase element using surface roughness and energy activation distribution is presented.

### Fabrication of High Precision PEMFC Membrane Electrode Assemblies by Sieve Printing Method

A. B. ANDRADE, M. L. MORA BEJARANO, E. F. CUNHA, E. ROBALINHO and M. LINARDI, *J. Fuel Cell Sci. Technol.*, 2009, 6, (2), 021305 (3 pages)

A sieve printing technique was used for the preparation of PEMFC gas diffusion electrodes. MEA evaluation was carried out in a 25 cm<sup>2</sup> single PEMFC with loadings of 0.4 mg Pt cm<sup>-2</sup> and 0.6 mg Pt cm<sup>-2</sup> on the anode and cathode, respectively. The MEAs had higher power density than spray printed ones.

### Synthesis of Intermetallic PtZn Nanoparticles by Reaction of Pt Nanoparticles with Zn Vapor and Their Application as Fuel Cell Catalysts

A. MIURA, H. WANG, B. M. LEONARD, H. D. ABRUÑA and F. J. DiSALVO, *Chem. Mater.*, 2009, 21, (13), 2661–2667

Intermetallic PtZn nanoparticles (1) were synthesised by reaction of C-supported Pt nanoparticles with Zn vapour at 500°C for 8 h under flowing N<sub>2</sub> at atmospheric pressure. The catalytic activities of supported (1) toward formic acid and MeOH electrooxidation were studied by differential electrochemical mass spectrometry. (1) exhibited higher currents for both oxidations than supported Pt nanoparticles with similar particle sizes.

## METALLURGY AND MATERIALS

### Facile Approach to the Synthesis of 3D Platinum Nanoflowers and Their Electrochemical Characteristics

J. N. TIWARI, F.-M. PAN and K.-L. LIN, *New J. Chem.*, 2009, 33, (7), 1482–1485

3D Pt nanoflowers (1) were synthesised by a potentiostatic pulse plating method on a Si substrate. Electrochemical analysis established that (1) had a much larger active surface area than a Pt thin film by a factor of > 110, and were likely preferentially oriented in the (100) and (110) surface planes. (1) exhibited excellent electrocatalytic activity toward MeOH oxidation and a high CO tolerance as compared with a Pt thin film.

### Fe Oxidation versus Pt Segregation in FePt Nanoparticles and Thin Films

L. HAN, U. WIEDWALD, B. KUERBANJIANG and P. ZIEMANN, *Nanotechnology*, 2009, 20, (28), 285706 (7 pages)

The oxidation behaviour of differently sized FePt nanoparticles (1) was investigated by XPS and compared to a FePt reference film. For the as-prepared samples Fe<sup>3+</sup> is formed, becoming detectable for exposures to pure O<sub>2</sub> above 10<sup>6</sup> langmuir, while Pt<sup>0</sup> remains. After annealing at 650°C, large (1) as well as the reference film exhibited a 100–1000 times enhanced resistance against oxidation, whereas small (1) (diameter 5 nm) showed no such enhancement.

### Atomic-Level Pd–Au Alloying and Controllable Hydrogen-Absorption Properties in Size-Controlled Nanoparticles Synthesized by Hydrogen Reduction

H. KOBAYASHI, M. YAMAUCHI, R. IKEDA and H. KITAGAWA, *Chem. Commun.*, 2009, (32), 4806–4808

PVP-protected Pd nanoparticles were prepared from the alcoholic reduction of PdCl<sub>2</sub> in the presence of PVP. An aqueous solution of HAuCl<sub>4</sub> was added and the mixture was stirred under H<sub>2</sub> gas to form Pd–Au alloy nanoparticles. 20 at.% of Au in Pd suppressed H<sub>2</sub> absorption completely. The amount of H<sub>2</sub> absorption is controllable by low-concentration alloying with Au.

## APPARATUS AND TECHNIQUE

### Nanocomposite Based on Depositing Platinum Nanostructure onto Carbon Nanotubes through a One-Pot, Facile Synthesis Method for Amperometric Sensing

D. WEN, X. ZOU, Y. LIU, L. SHANG and S. DONG, *Talanta*, 2009, 79, (5), 1233–1237

Pt nanoparticles deposited onto carbon MWNTs, through direct chemical reduction, can electrocatalyse the oxidation of H<sub>2</sub>O<sub>2</sub> and substantially raise the response current. Glucose oxidase (GOD) was immobilised on the nanocomposite-based electrode with a thin layer of Nafion. This glucose biosensor with a GOD loading concentration of 10 mg ml<sup>-1</sup> had a detection limit of 3 μM and a response time of 3 s.

## BIOMEDICAL AND DENTAL

### Inhibition of Transcription by Platinum Antitumor Compounds

R. C. TODD and S. J. LIPPARD, *Metallomics*, 2009, 1, (4), 280–291

Structural investigations of Pt–DNA adducts and the effects of these lesions on global DNA geometry are reviewed. Research detailing inhibition of cellular transcription by Pt–DNA adducts is presented. A mechanistic analysis of how DNA structural distortions induced by Pt damage may inhibit RNA synthesis *in vivo* was carried out. (155 Refs.)

## CHEMISTRY

### Synthesis and Structural Characterization of Binuclear Palladium(II) Complexes of Salicylaldimine Dithiosemicarbazones

T. STRINGER, P. CHELLAN, B. THERRIEN, N. SHUNMOOGAM-GOUNDEN, D. T. HENDRICKS and G. S. SMITH, *Polyhedron*, 2009, 28, (14), 2839–2846

The title complexes were synthesised by the reaction of ethylene- and phenylene-bridged dithiosemicarbazones with Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>. Two representative Pd complexes were characterised by XRD. The two Pd centres are coordinated in a slightly distorted square-planar geometry, which gives rise in each case to five- and six-membered chelate rings. The ligands coordinate to Pd in a tridentate manner, through the phenolic O, imine N and thiolate S atoms.

### Synthesis, Properties and Crystal Structures of Volatile β-Ketoiminate Pd Complexes, Precursors for Palladium Chemical Vapor Deposition

G. I. ZHARKOVA, P. A. STABNIKOV, I. A. BAIDINA, A. I. SMOLENTSEV and S. V. TKACHEV, *Polyhedron*, 2009, 28, (12), 2307–2312

β-Aminovinylketone ligands CH<sub>3</sub>C(NH<sub>2</sub>)CHC(O)CH<sub>3</sub> and CH<sub>3</sub>C(NHCH<sub>3</sub>)CHC(O)CH<sub>3</sub> were synthesised. Their reaction with PdCl<sub>2</sub> in an amine medium afforded the complexes Pd[CH<sub>3</sub>C(NH)CHC(O)CH<sub>3</sub>]<sub>2</sub> (1) and Pd[CH<sub>3</sub>C(NCH<sub>3</sub>)CHC(O)CH<sub>3</sub>]<sub>2</sub> (2). In (1) and (2), the Pd atom exhibits square coordination, Pd O<sub>2</sub>N<sub>2</sub>.