

# Abstracts

## CATALYSIS – APPLIED AND PHYSICAL ASPECTS

### On the Key Role of Hydroxyl Groups in Platinum-Catalysed Alcohol Oxidation in Aqueous Medium

S. Chibani, C. Michel, F. Delbecq, C. Pinel and M. Besson, *Catal. Sci. Technol.*, 2013, **3**, (2), 339–350

In the aerobic selective oxidation of alcohols in aqueous medium in a batch reactor, the addition of H<sub>2</sub>O to dioxane solvent (10–50 vol%) substantially increased the activity of a Pt/C catalyst. Periodic DFT calculations were performed to compare the reactivity of alcohols on the bare Pt(111) surface and in the presence of adsorbed H<sub>2</sub>O or OH groups. The calculations were found to indicate that the presence of adsorbed OH groups promotes catalytic activity by participating directly in the catalytic pathways and reducing the activation barrier. Decarbonylation of acetaldehyde at 373 K is thought to be the cause of deactivation of the catalyst.

### Recyclable Pd-Incorporated Perovskite-Titanate Catalysts Synthesized in Molten Salts for the Liquid-Phase Oxidation of Alcohols with Molecular Oxygen

I. B. Adilina, T. Hara, N. Ichikuni, N. Kumada and S. Shimazu, *Bull. Chem. Soc. Jpn.*, 2013, **86**, (1), 146–152

Pd-incorporated titanate catalysts (Pd/KSTO) were prepared by the intercalation of Pd(NO<sub>3</sub>)<sub>2</sub> into layered potassium titanate (KTO), which proceeded *via* a cation-exchange reaction in molten salts. Perovskite phases of Pd/KSTO were obtained at 600°C and above, whereas a lepidocrocite-type layered titanate structure, similar to that of KTO, was retained at 400°C. The Pd/KSTO catalysts were then investigated for the liquid-phase oxidation of alcohols using molecular O<sub>2</sub>. The perovskite-type Pd/KSTO catalyst, exhibited superior activity, giving a high TON of 800 in the aerobic oxidation of 1-phenylethanol with no loss of catalytic activity after three runs.

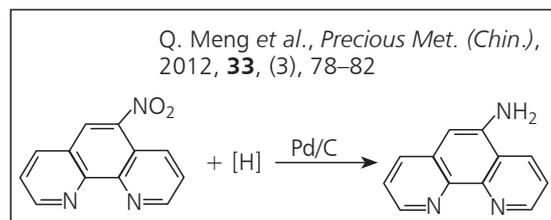
## CATALYSIS – INDUSTRIAL PROCESS

### Application of Precious Metal Catalysts in Drug Synthesis

Q. Meng, Q. Ye, W. Liu and Y. Wang, *Precious Met. (Chin.)*, 2012, **33**, (3), 78–82

Supported pgm catalysts (e.g. Pd/Al<sub>2</sub>O<sub>3</sub>, Pd/C, Pd-Co/C

and Ru/C) with high activity and high selectivity are widely used in the pharmaceutical as well as the fine chemicals industry. The application of these catalysts in drug synthetic reactions including coupling, hydroformylation, hydrogenolysis, hydrosilylation, isomerisation and transfer hydrogenation is described. (Contains 25 references.)



## CATALYSIS – REACTIONS

### Aqueous Phase Transfer Hydrogenation of Aryl Ketones Catalysed by Achiral Ruthenium(II) and Rhodium(III) Complexes and Their Papain Conjugates

N. Madern, B. Talbi and M. Salmay, *Appl. Organomet. Chem.*, 2013, **27**, (1), 6–12

Ru and Rh complexes having 2,2'-dipyridylamine ligands substituted at the central N atom by an alkyl chain terminated by a maleimide functional group were evaluated along with a Rh(III) complex of unsubstituted 2,2'-dipyridylamine as catalysts in the transfer hydrogenation of aryl ketones in H<sub>2</sub>O with formate as hydrogen donor. All of the complexes except one led to secondary alcohol products. Site-specific anchoring of the *N*-maleimide complexes to the single free cysteine residue of the cysteine endoproteinase papain endowed this protein with transfer hydrogenase properties towards 2,2,2-trifluoroacetophenone.

## EMISSIONS CONTROL

### Effect of Barium Sulfate on Sulfur Resistance of Pt/Ce<sub>0.4</sub>Zr<sub>0.6</sub>O<sub>2</sub> Catalyst

Y. Zheng, Y. Zheng, Y. Xiao, G. Cai and K.-M. Wei, *Catal. Commun.*, 2012, **27**, 189–192

BaSO<sub>4</sub>-doped ceria zirconia (CZ) solid solution was prepared using a coprecipitation method. The synthesised samples were used as supports for preparing Pt catalysts. BaSO<sub>4</sub> was evenly distributed in the irregular mesoporous structure of the CZ. Furthermore, the addition of BaSO<sub>4</sub> to the CZ improved

the desorption of sulfur species under a reducing atmosphere, which could decrease the accumulation of sulfur species in the catalyst. The sulfur poisoning resistance of the catalyst was thereby improved.

## FUEL CELLS

### Platinum Catalysts Supported on Nafion Functionalized Carbon Black for Fuel Cell Application

F. Luo, S. Liao and D. Chen, *J. Energy Chem.*, 2013, **22**, (1), 87–92

A Pt/Nafion functionalised C black catalyst was characterised by IR spectroscopy, TEM and XRD. TEM showed that the active Pt component was in the form of NPs and highly dispersed on the carbon black. The catalyst showed improved activity towards methanol anodic oxidation and the ORR, resulting from the high dispersion of the active Pt component. The catalyst produced an increase in the electrochemically accessible surface area and ion channels, as well as easier charge-transfer at the polymer/electrolyte interface.

### Three-Dimensional Tracking and Visualization of Hundreds of Pt–Co Fuel Cell Nanocatalysts during Electrochemical Aging

Y. Yu, H. L. Xin, R. Hovden, D. Wang, E. D. Rus, J. A. Mundy, D. A. Muller and H. D. Abruña, *Nano Lett.*, 2012, **12**, (9), 4417–4423

A 3D tomographic method for tracking the trajectories and morphological changes of individual Pt-Co nanocatalyst particles on a fuel cell C support, before and after electrochemical ageing *via* potential sweeps, was developed. The growth in the Pt shell thickness and observation of coalescence in 3D are proposed to explain the decrease in electrochemically active surface area and the loss of activity of Pt-Co nanocatalysts in PEMFC cathodes. Along with atomic-scale EELS imaging, the experiment enables the correlation of catalyst performance degradation with changes in particle/interparticle morphologies, particle–support interactions and the near-surface chemical composition.

### SiO<sub>2</sub>–RuO<sub>2</sub>: A Stable Electrocatalyst Support

C.-P. Lo and V. Ramani, *ACS Appl. Mater. Interfaces*, 2012, **4**, (11), 6109–6116

High surface area SiO<sub>2</sub>–RuO<sub>2</sub> (SRO) supports were obtained using a wet chemical method. Pt NPs were deposited on their surface. The optimal 1:1 mol ratio of SiO<sub>2</sub>–RuO<sub>2</sub> (SRO-1) had a BET

surface area of 305 m<sup>2</sup> g<sup>-1</sup> and an electrical conductivity of 24 S cm<sup>-1</sup>. SRO-1 demonstrated 10-fold higher electrochemical stability than Vulcan XC-72RC when subjected to an aggressive accelerated stability test. The mass activity of Pt-doped SRO-1 was 54 mA mg<sub>Pt</sub><sup>-1</sup>, whereas its specific activity was 115 μA cm<sub>Pt</sub><sup>-2</sup>. The fuel cell performance obtained with this catalyst was lower, but compared favourably against commercial Pt/C.

## APPARATUS AND TECHNIQUE

### Preparation of Pd–Pt Co-Loaded TiO<sub>2</sub> Thin Films by Sol-Gel Method for Hydrogen Gas Sensing

S. Yanagida, M. Makino, T. Ogaki and A. Yasumori, *J. Electrochem. Soc.*, 2012, **159**, (12), B845–B849

Pd-, Pt- and Pd–Pt-loaded TiO<sub>2</sub> thin films were prepared and their respective capabilities as H<sub>2</sub> gas combustion sensors were investigated. H<sub>2</sub> gas sensing was assessed at 300°C by measuring the sample resistance under H<sub>2</sub> gas (3%–100%) and air flow conditions. The Pd–Pt step-by-step loaded sample showed higher sensitivity than either the Pd or Pt single-loaded sample for H<sub>2</sub> concentrations of less than 30 vol%. STEM revealed its structure: Pt fine particles deposited selectively on the Pd particles predeposited on the TiO<sub>2</sub> surface.

## ELECTROCHEMISTRY

### A Kinetic Description of Pd Electrodeposition under Mixed Control of Charge Transfer and Diffusion

M. Rezaei, S. H. Tabaian and D. F. Haghshenas, *J. Electroanal. Chem.*, 2012, **687**, 95–101

The electrodeposition of Pd from an aqueous solution containing PdCl<sub>2</sub> (0.001 M) and H<sub>2</sub>SO<sub>4</sub> (0.5 M) was studied by CV and potentiostatic current-time transients (CTTs). From the polarisation curves, regions corresponding to charge transfer control, mixed control and diffusion control were identified. In the mixed control region, the CTTs results suggested processes involving adsorption, the ion transfer reaction and 3D progressive nucleation with mixed charge transfer-diffusion controlled growth. The analysis of CTTs at short times was performed with the model proposed by Milchev and Zapryanova. The reduction reaction of Pd(II) → Pd(I), as an ion transfer reaction, occurs before the formation of the Pd nucleus.

## PHOTOCONVERSION

### Porous, Platinum Nanoparticle-Adsorbed Carbon Nanotube Yarns for Efficient Fiber Solar Cells

S. Zhang, C. Ji, Z. Bian, P. Yu, L. Zhang, D. Liu, E. Shi, Y. Shang, H. Peng, Q. Cheng, D. Wang, C. Huang and A. Cao, *ACS Nano*, 2012, **6**, (8), 7191–7198

A Pt NP-adsorbed C nanotube yarn was obtained by solution adsorption and yarn spinning processes, with uniformly dispersed Pt NPs throughout the porous nanotube network. TiO<sub>2</sub>-based dye-sensitised fibre solar cells with a Pt-nanotube hybrid yarn as counter electrode were fabricated. A power conversion efficiency of 4.85% under standard illumination (AM1.5, 100 mW cm<sup>-2</sup>) was achieved, comparable to the same type of fibre cells with a Pt wire electrode (4.23%).

### Photochemistry between a Ruthenium(II) Pyridylimidazole Complex and Benzoquinone: Simple Electron Transfer versus Proton-Coupled Electron Transfer

R. Hönes, M. Kuss-Petermann and O. S. Wenger, *Photochem. Photobiol. Sci.*, 2013, **12**, (2), 254–261

A Ru(II) complex with two 4,4'-bis(trifluoromethyl)-2,2'-bipyridine chelates and a 2-(2'-pyridyl)imidazole ligand was synthesised. The proton-coupled electron transfer (PCET) between the Ru(II) complex and 1,4-benzoquinone as an electron/proton acceptor was investigated by spectroscopic means. Excited-state deactivation was found to occur predominantly *via* simple oxidative quenching, but a minor fraction of the photoexcited complex was thought to have reacted *via* PCET.

## REFINING AND RECOVERY

### Selective Recovery of Precious Metals from Acidic Leach Liquor of Circuit Boards of Spent Mobile Phones Using Chemically Modified Persimmon Tannin Gel

M. Gurung, B. B. Adhikari, H. Kawakita, K. Ohto, K. Inoue and S. Alam, *Ind. Eng. Chem. Res.*, 2012, **51**, (37), 11901–11913

A tannin-based adsorbent was prepared by immobilising bithiourea on persimmon tannin extract. The gel exhibited selectivity for precious metal ions such as Au(III), Pd(II) and Pt(IV) over base metal ions such as Cu(II), Fe(III), Ni(II) and Zn(II) in 1–5 mol dm<sup>-3</sup> HCl. The real time applicability of the gel for the recovery of precious metals was demonstrated

for the acidic leach liquor of PCBs from spent mobile phones.

### In Situ Platinum Recovery and Color Removal from Organosilicon Streams

H. Bai, *Ind. Eng. Chem. Res.*, 2012, **51**, (50), 16457–16466

The recovery of Pt from organosilicon hydrosilylation streams is a potential source of cost savings. Here *in situ* fixed-bed adsorption technology was demonstrated to be effective for Pt recovery and product colour removal. With the *in situ* Pt recovery process and using a functionalised silica gel scavenging material, a Pt recovery >90% was achieved both from silane distillation heavy wastes (with initial Pt concentration of ~50 ppm) and from organosilicon products (with initial Pt concentration of ~5 ppm).