

# Abstracts

## CATALYSIS – APPLIED AND PHYSICAL ASPECTS

### Mild Synthesis of Mesoporous Silica Supported Ruthenium Nanoparticles as Heterogeneous Catalysts in Oxidative Wittig Coupling Reactions

A. L. Carrillo, L. C. Schmidt, M. L. Marín and J. C. Scaiano, *Catal. Sci. Technol.*, 2014, Advance Article

A new efficient approach for *in situ* synthesis of anchored ruthenium nanoparticles (RuNPs) in three different kinds of mesoporous silica materials (MCM-41, SBA-15 and HMS) has been developed. The solids were synthesised under very mild conditions from  $\text{RuCl}_3 \cdot \text{H}_2\text{O}$  salt reduced in 1 h at room temperature in the mesoporous silicas grafted with aminopropyltriethoxysilane (APTES). The Ru nanoparticles were well dispersed with an average size of 3 nm. These materials have a molar ratio of Si:Ru = 40.

### Porous MOFs Supported Palladium Catalysts for Phenol Hydrogenation: A Comparative Study on MIL-101 and MIL-53

D. Zhang, Y. Guan, E. J. M. Hensen, L. Chen and Y. Wang, *Catal. Commun.*, 2013, 41, 47–51

Two metal organic frameworks, chromium benzenedicarboxylates MIL-101 and MIL-53 were synthesised and used as supports for Pd catalysts. MIL-101 is highly hydrophilic and beneficial as support for fine Pd nanoparticles, of average size 2.3 nm. Microporous MIL-53 is relatively hydrophobic and larger Pd particles of 4.3 nm formed on the external surface. The phenol adsorption behaviours on the MILs were studied with different initial phenol concentrations (0.05 M, 0.1 M, 0.15 M, 0.2 M and 0.25 M) at 20°C to compare surface hydrophobicity. Pd/MIL-101 showed better phenol selective hydrogenation activity to cyclohexanone (>98%) under mild reaction conditions. The results show that MIL-101 is superior to the MIL-53 as a support when aqueous  $\text{PdCl}_2$  is used as a precursor.

## CATALYSIS – INDUSTRIAL PROCESS

### Characterization and Performance of the Bifunctional Platinum-Loaded Calcium-Hydroxyapatite in the One-Step Synthesis of Methyl Isobutyl Ketone

N. Takarroumt, M. Kacimi, F. Bozon-Verduraz, L. F. Liotta and M. Ziyad, *J. Mol. Catal. A: Chem.*, 2013, 377, 42–50

Ca-hydroxyapatite catalysts loaded with different amounts of Pt(Pt(x)/CaHAp) were synthesised and characterised by  $\text{N}_2$ -adsorption, XRD, TEM, FTIR, UV-VIS-NIR spectroscopy and TPR. The loaded Pt exchanged and dispersed on the apatite surface, forming particles of average size 2 nm. The specific surface area of CaHAp decreased as Pt loading increased. The catalysts were tested for dehydrogenation of butan-2-ol into MEK. The important activity at low temperatures was attributed to Pt and  $\text{Pt}^{2+}$  species associated with the basic  $\text{Ca}^{2+}\text{-O}^{2-}$  groups of the apatite. Optimal performance for acetone conversion to MIBK was achieved with sample loaded with 0.5 wt% Pt. At 150°C and stationary state a MIBK yield of 23% was obtained with a selectivity of 74%. All the Pt(x)/CaHAp catalysts showed acceptable stability over time on stream with no production of heavy compounds.

## CATALYSIS – REACTIONS

### Poly (Styrene-co-Divinylbenzene) Amine Functionalized Polymer Supported Ruthenium Nanoparticles Catalyst Active in Hydrogenation of Xylose

D. K. Mishra, A. A. Dabbawala and J. Hwang, *Catal. Commun.*, 2013, 41, 52–55

The title catalyst has been evaluated for the first time in hydrogenation of xylose to xylitol. The Ru/PSN catalyst was characterised by XRD, TEM and CO chemisorption. Experiments were carried out using the catalyst with different Ru loading of 1.0–3.0%, at different temperatures of 100–400°C under different  $\text{H}_2$  pressures of 30–55 bar and with varying stirring speeds from 400–1200 rpm. The catalyst could be reused up to four times.

### An Effective Strategy for Immobilizing a Homogeneous Palladium Complex onto Silica: Efficient and Reusable Catalyst for Suzuki-Miyaura Reactions

C. Sarmah, D. Sahu and P. Das, *Catal. Commun.*, 2013, 41, 75–78

A strategy to immobilise a homogeneous Pd complex onto silica gel by introducing 4-pyridinecarbaldehyde into the coordination sphere of Pd has been investigated. The material was characterised by FTIR,

BET measurements, XRD, SEM-EDX and ICP-AES. The supported material is an efficient catalyst for the Suzuki-Miyaura reactions of aryl halides with low Pd loading, 0.04 mol%, in an environmentally friendly reaction. The reaction proceeded smoothly and 96% 4-methoxybiphenyl was isolated after 6 h reaction time.

#### Ruthenium-Catalyzed *ortho*-C-H Halogenations of Benzamides

L. Wang and L. Ackermann, *Chem. Commun.*, 2014, **50**, (9), 1083–1085

The first Ru-catalysed *ortho*-selective C–H halogenations on arenes through C–H activation are reported. A catalytic system of Ru<sub>3</sub>(CO)<sub>12</sub> and Ag<sub>2</sub>O<sub>2</sub>C(1-Ad) allowed site-selective brominations and iodinations on amides with ample scope and excellent functional group tolerance. Preliminary mechanistic studies provided evidence for a reversible C–H metallation event.

## EMISSIONS CONTROL

#### Self-Regeneration of Three-Way Catalyst Rhodium Supported on La-Containing ZrO<sub>2</sub> in an Oxidative Atmosphere

H. Kawabata, Y. Koda, H. Sumida, M. Shigetsu, A. Takami and K. Inumaru, *Catal. Sci. Technol.*, 2013, Accepted Manuscript

Rh supported on lanthanoid (La, Ce, Pr or Nd)-containing ZrO<sub>2</sub> was investigated as a TWC, following an ageing treatment by oxidation at 1273 K to simulate 80,000 km in real vehicles. The properties of Rh were assessed by TEM, CO chemisorption and TPR using CO. The aged catalyst exhibited superior activity for the steam reforming reaction. The hydrogen produced reduced the previously oxidised Rh in Rh/Zr-La-O, regenerating the catalyst. The results highlight the potential of the present strategy for developing active TWC with high tolerance to

oxidative conditions. The Rh particles supported on Zr-La-O maintained their low oxidation state during the reaction.

## FUEL CELLS

#### The Electrooxidation Mechanism of Formic Acid on Platinum and on Lead ad-Atoms Modified Platinum Studied with the Kinetic Isotope Effect

M. Bęłowska-Brzezinska, T. Łuczak, J. Stelmach and R. Holze, *J. Power Sources*, 2014, **251**, 30–37

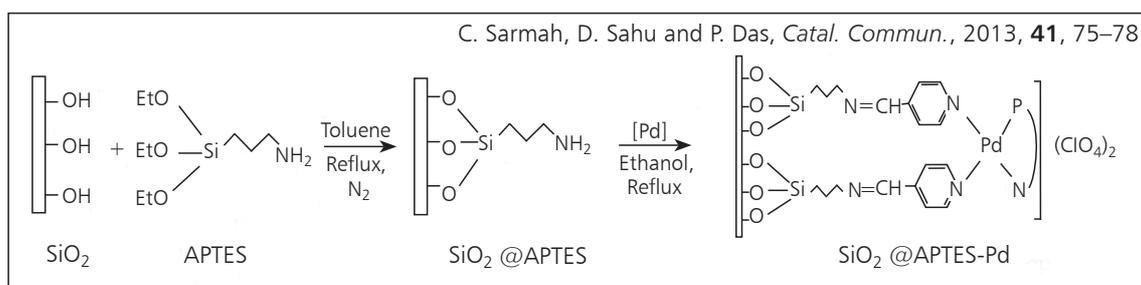
Poisoning of the electrode surface by CO-like species was prevented by suppression of dissociative chemisorption of FA due to a fast competitive underpotential deposition of lead ad-atoms on the Pt surface from an acidic solution containing Pb<sup>2+</sup> cations. HCOOH was oxidised 8.5 times faster on a Pt/Pb electrode than DCOOD. C–H and O–H bonds were shown to be simultaneously cleaved in the rate determining step. C–H bond cleavage was found to be accomplished by C–OH and not O–H bond split during FA decomposition.

## PHOTOCONVERSION

#### A Simple Synthetic Route to Obtain Pure Trans-Ruthenium(II) Complexes for Dye-Sensitized Solar Cell Applications

C. Barolo, J. H. Yum, E. Artuso, N. Barbero, D. Di Censo, M. G. Lobello, S. Fantacci, F. De Angelis, M. Grätzel, M. K. Nazeeruddin and G. Viscardi, *ChemSusChem.*, 2013, **6**, (11), 2170–2180

A synthetic route to obtain a functionalised quaterpyridine ligand and its *trans*-dithiocyanato Ru complex based on a microwave-assisted procedure is presented. This Ru and quaterpyridine ligand complex is used as a sensitizer in dye-sensitized solar cells yielding a short circuit photocurrent density of >19 mA cm<sup>-2</sup> with broad incident photon to current



conversion efficiency spectra ranging from 400–900 nm, exceeding 80% at 700 nm.

## CHEMISTRY

### Growth of Concave Polyhedral Pd Nanocrystals with 32 Facets through *in situ* Facet-Selective Etching

Z.-c. Zhang, F. Nosheen, J.-c. Zhang, Y. Yang, P.-p. Wang, J. Zhuang and X. Wang, *ChemSusChem*, 2013, **6**, (10), 1893–1897

Concave Pd polyhedra have been successfully prepared by selectively etching the {100} facets *in situ* by  $\Gamma^-$  ions. Due to the presence of a high density of atomic steps and surface relaxation, the concave Pd polyhedra exhibit an enhanced electrocatalytic activity towards ethanol oxidation.

## ELECTRONICS

### Efficient Electronic Communication of Two Ruthenium Centers through a Rigid Ditopic N-Heterocyclic Carbene Linker

M. Nussbaum, O. Schuster and M. Albrecht, *Chem. Eur. J.*, 2013, **19**, (51), 17517–17527

A ditopic benzobis(carbene) ligand precursor containing a chelating pyridyl moiety was prepared and used to obtain bimetallic Ru complexes by transmetalation. The two metal centres were found to be electronically decoupled when the Ru is in a pseudotetrahedral geometry imparted by a cymene spectator ligand. Ligand exchange of the  $\text{Cl}^-$ /cymene ligands for two bipyridine or four MeCN ligands induced a change of the coordination geometry to octahedral. As a consequence, the Ru centres, separated through space by more than 10 Å, became electronically coupled, evidenced by two different metal-centred oxidation processes. These results demonstrate the efficiency of carbenes and, in particular, of the bbi ligand scaffold for mediating electron transfer and for the fabrication of molecular redox switches.

## ELECTROCHEMISTRY

### Activation of Nickel for Hydrogen Evolution by Spontaneous Deposition of Iridium

M. Duca, E. Guerrini, A. Colombo and S. Trasatti, *Electrocatalysis*, 2013, **4**, (4), 338–345

Activation of Ni electrodes was performed by deposition of Ir from HCl solutions of  $\text{IrCl}_2$ . Efficiency

of deposition was dependent on precursor and aqueous solution ageing. Cyclic voltammetry showed hydrogen de/adsorption peaks with magnitude proportional to the amount of Ir deposited. Tafel plots showed slope decrease from 120 mV, typical of bare Ni, down to 40 mV typical of pure Ir.

## MEDICAL

### Cyclic RGD-Linked Polymeric Micelles for Targeted Delivery of Platinum Anticancer Drugs to Glioblastoma through the Blood-Brain Tumor Barrier

Y. Miura, T. Takenaka, K. Toh, S. Wu, H. Nishihara, M. R. Kano, Y. Ino, T. Nomoto, Y. Matsumoto, H. Koyama, H. Cabral, N. Nishiyama and K. Kataoka, *ACS Nano*, 2013, **7**, (10), 8583–8592

A highly efficient drug delivery to intractable human glioblastoma (U87MG) tumours has been achieved by using a Pt anticancer drug incorporating polymeric micelle with cyclic Arg-Gly-Asp (cRGD) ligand molecules. A rapid accumulation and high permeability from vessels into the tumour parenchyma was revealed. The selective and accelerated accumulation of cRGD/m into tumours occurred *via* an active internalisation pathway (possibly transcytosis), thereby producing significant antitumour effects in an orthotopic mouse model of U87MG human glioblastoma.

## NANOTECHNOLOGY

### Pure Platinum Nanostructures Grown by Electron Beam Induced Deposition

C. Elbadawi, M. Toth and C. J. Lobo, *ACS Appl. Mater. Interfaces.*, 2013, **5**, (19), 9372–9376

A method for localised, mask free deposition of high-purity Pt employs room-temperature, direct-write EBID using the precursor  $\text{Pt}(\text{PF}_3)_4$ , and a low temperature ( $\leq 400^\circ\text{C}$ ) postgrowth annealing in  $\text{H}_2\text{O}$ . This annealing removes phosphorus contaminants. The resulting Pt is indistinguishable from pure Pt films by WDS.

## PHYSICAL METHODS

### Osmium Isotope Evidence for a Large Late Triassic Impact Event

H. Sato, T. Onoue, T. Nozaki and K. Suzuki, *Nature Commun.*, 2013, **4**, 2455

A report on the Os isotope fingerprint of an

extraterrestrial impact from Upper Triassic chert successions in Japan is presented. Os isotope data exhibit a marked negative excursion from an initial Os isotope ratio ( $^{187}\text{Os}/^{188}\text{Os}_i$ ) of  $\sim 0.477$  to unradiogenic values of  $\sim 0.126$  in a PGE-enriched claystone layer. The timing of the Os isotope excursion coincides with both elevated Os concentrations and low Re:Os ratios. The magnitude of this negative Os isotope excursion is comparable to those found at Cretaceous-Paleogene boundary sites. The geochemical lines of evidence demonstrate that a large impactor of 3.3–7.8 km in diameter, produced a global decrease in seawater  $^{187}\text{Os}/^{188}\text{Os}$  ratios in the late Triassic.