

# Abstracts

## CATALYSIS – INDUSTRIAL PROCESS

### Development of Preformed Pd Catalysts for Cross-Coupling Reactions, Beyond the 2010 Nobel Prize

H. Li, C. C. C. Johansson Seechurn and T. J. Colacot, *ACS Catal.*, 2012, **2**, (6), 1147–1164

Strategies for the development of Pd catalysts based on  $L_2Pd$  and  $LPd$  species, beyond the contributions of the 2010 chemistry Nobel laureates Heck, Negishi and Suzuki are reviewed. Well-defined, preformed Pd catalysts improve the selectivity and activity of cross-coupling reactions by reducing metal loading and ligand:metal ratios. This review describes the development of Pd precatalysts over the last ten years and highlights the benefits of using well-defined preformed catalysts relative to those generated *in situ*. It is concluded that new catalyst development can significantly expand the scope of these highly valued organic transformations. (Contains 145 references.)

### Palladium-Catalyzed Cross-Coupling: A Historical Contextual Perspective to the 2010 Nobel Prize

C. C. C. Johansson Seechurn, M. O. Kitching, T. J. Colacot and V. Snieckus, *Angew. Chem. Int. Ed.*, 2012, **51**, (21), 5062–5085

This review attempts to trace the historical origin of the powerful Pd-catalysed C–C bond construction reactions, and outlines developments from the seminal discoveries leading to their eminent position today. Syntheses of natural products and drug molecules where the key step(s) consist of Pd-catalysed cross-couplings include the synthesis

of losartan, the Merck Singulair<sup>®</sup> process, the total synthesis of discodermolide and the Novartis route to Gleevec<sup>®</sup> (imatinib). Unsolved problems, challenges and outlook for metal-catalysed cross-couplings are also discussed. (Contains 194 references.)

## CATALYSIS – REACTIONS

### Ion-Paired Chiral Ligands for Asymmetric Palladium Catalysis

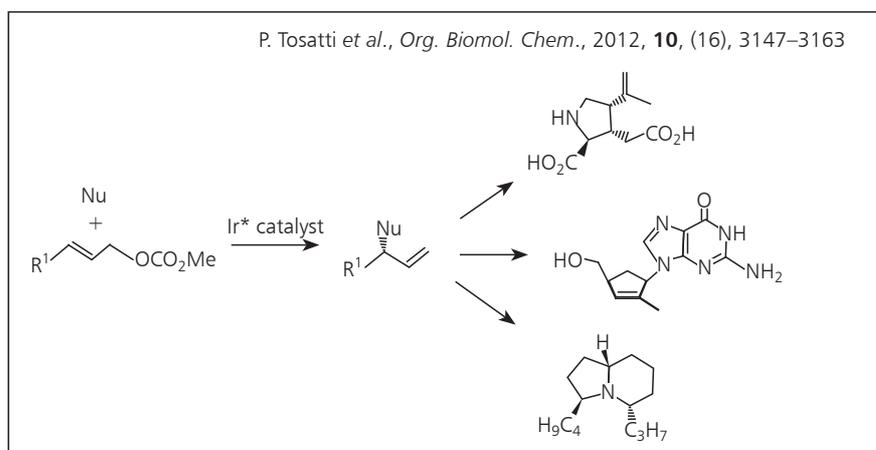
K. Ohmatsu, M. Ito, T. Kunieda and T. Ooi, *Nature Chem.*, 2012, **4**, (6), 473–477

An achiral cationic ammonium–phosphine hybrid ligand paired with a chiral binaphtholate anion has been designed. This ion-paired chiral ligand gives a remarkable stereocontrolling ability to its Pd complex (prepared from  $Pd_2(dba)_3$ ), which catalyses a highly enantioselective allylic alkylation of  $\alpha$ -nitrocarboxylates. By exploiting the possible combinations of the achiral onium entities with suitable coordinative functionalities and readily available chiral acids, this approach could contribute to the development of a range of metal-catalysed, stereoselective chemical transformations.

### Recent Advances and Applications of Iridium-Catalysed Asymmetric Allylic Substitution

P. Tosatti, A. Nelson and S. P. Marsden, *Org. Biomol. Chem.*, 2012, **10**, (16), 3147–3163

The development of chiral Ir catalysts for asymmetric allylic substitution reactions and their application to the synthesis of natural products and other biologically relevant compounds is reviewed. Since their discovery in 1997, Ir-catalysed asymmetric allylic substitutions



have developed into a powerful tool for the synthesis of chiral building blocks *via* C–C and C–heteroatom bond formation. This overviews the development of Ir catalysts derived from an Ir salt and a chiral phosphoramidite. (Contains 78 references.)

## EMISSIONS CONTROL

### Efficient Degradation of TCE in Groundwater Using Pd and Electro-generated H<sub>2</sub> and O<sub>2</sub>: A Shift in Pathway from Hydrodechlorination to Oxidation in the Presence of Ferrous Ions

S. Yuan, X. Mao and A. N. Alshwabkeh, *Environ. Sci. Technol.*, 2012, **46**, (6), 3398–3405

Degradation of TCE in simulated groundwater by 1% wt Pd/Al<sub>2</sub>O<sub>3</sub> and electrogenerated H<sub>2</sub> and O<sub>2</sub> was investigated. Oxidation of TCE in the presence of Fe(II) is significantly more efficient than hydrodechlorination in the absence of Fe(II) under weak acidic conditions. Complete dechlorination is achieved with the formation of nontoxic organic acids and CO<sub>2</sub>. A novel Pd-based electrochemical process is proposed for groundwater remediation.

### Catalytic Ozonation of Oxalate with a Cerium Supported Palladium Oxide: An Efficient Degradation Not Relying on Hydroxyl Radical Oxidation

T. Zhang, W. Li and J.-P. Croué, *Environ. Sci. Technol.*, 2011, **45**, (21), 9339–9346

PdO/CeO<sub>2</sub> at a low Pd loading was very effective in catalytic ozonation of oxalate. The oxalate was degraded into CO<sub>2</sub>. The catalyst was highly active and selective for oxalate degradation in water. ATR-FTIR and *in situ* Raman spectroscopy revealed that oxalate was adsorbed on the CeO<sub>2</sub> forming surface complexes, and O<sub>3</sub> was adsorbed on the PdO and further decomposed to surface atomic O, surface peroxide and O<sub>2</sub> gas in sequence.

## FUEL CELLS

### Alcohol Crossover Behavior in Direct Alcohol Fuel Cells (DAFCs) System

Y. H. Chu and Y. G. Shul, *Fuel Cells*, 2012, **12**, (1), 109–115

The alcohols (methanol, ethanol and 1-propanol) crossover behaviour of through MEA in DAFC was studied. The crossover rate decreased when the molecular chain length of alcohol became longer. The effect of the electrodes (60% Pt-Ru/C anode; 60% Pt/C cathode) to hinder crossover rate of MeOH

was studied. The anode hinders the crossover rate of the alcohol. At below 100°C, physical blocking effect was dominant to alcohol oxidation rate to reduce alcohol crossover, but over 100°C, MeOH oxidation rate superior to physical blocking effect.

### Nanoporous Surface Alloys as Highly Active and Durable Oxygen Reduction Reaction Electrocatalysts

R. Wang, C. Xu, X. Bi and Y. Ding, *Energy Environ. Sci.*, 2012, **5**, (1), 5281–5286

Nanoporous Pt/Ni alloys with nearly pure Pt surface and alloy core were obtained by a two-step dealloying process; they exhibit improved durability and activity toward ORR as compared to the Pt/C catalyst. Nanoporous-Pt<sub>1</sub>Ni<sub>1</sub> alloys were first fabricated by dealloying Pt/Ni/Al alloy foils in 0.5 M NaOH solution at rt for 48 h. Then nanoporous-Pt<sub>1</sub>Ni<sub>1</sub> alloys were further treated in dilute HNO<sub>3</sub> (0.7 M) at rt for 30 min to prepare nanoporous surface alloys (nanoporous-Pt<sub>6</sub>Ni<sub>1</sub>). The products were washed several times with ultrapure water and dried at rt.

## APPARATUS AND TECHNIQUE

### A Voltammetric Electronic Tongue as Tool for Water Quality Monitoring in Wastewater Treatment Plants

I. Campos, M. Alcañiz, D. Aguado, R. Barat, J. Ferrer, L. Gil, M. Marrakchi, R. Martínez-Mañez, J. Soto and J.-L. Vivancos, *Water Res.*, 2012, **46**, (8), 2605–2614

A voltammetric electronic tongue can be used for the determination of water quality parameters from influent and effluent wastewater from a Submerged Anaerobic Membrane Bioreactor pilot plant. The electronic tongue consists of a set of noble (Au, Pt, Rh, Ir and Ag) and non-noble (Ni, Co and Cu) electrodes housed inside a stainless steel cylinder. The electronic tongue could be used for the determination of soluble biological oxygen demand (BOD), soluble chemical oxygen demand (COD), ammonia (NH<sub>4</sub>-N), orthophosphate (PO<sub>4</sub>-P), sulfate (SO<sub>4</sub>-S) and alkalinity.

### Real-Time DNA Detection Using Pt Nanoparticle-Decorated Reduced Graphene Oxide Field-Effect Transistors

Z. Yin, Q. He, X. Huang, J. Zhang, S. Wu, P. Chen, G. Lu, P. Chen, Q. Zhang, Q. Yan and H. Zhang, *Nanoscale*, 2012, **4**, (1), 293–297

A large-area, continuous, few-layer reduced graphene oxide (rGO) thin film was fabricated on a Si/SiO<sub>2</sub> wafer

using the Langmuir–Blodgett method followed by thermal reduction. After photochemical reduction of Pt NPs on the rGO, the obtained Pt NPs/rGO composite was used as the conductive channel in a solution-gated field effect transistor. Real-time detection of hybridisation of single-stranded DNA with high sensitivity was achievable.

## CHEMISTRY

### An Unexpected Triammine(oxalato)platinum(II) Complex Obtained from the Aqueous Solution of Tetraammineplatinum(II) Oxalate

X.-Z. Chen, Q.-S. Ye, M.-J. Xie, J.-L. Chen, Z.-F. Pan and W.-P. Liu, *Res. Chem. Intermed.*, 2012, **38**, (2), 421–428

Triammine(oxalato)platinum(II) in which the oxalate anion acts as a monodentate ligand, was isolated when recrystallising  $[\text{Pt}(\text{NH}_3)_4](\text{C}_2\text{O}_4)$ . Single crystal XRD study showed that the Pt(II) atom is coordinated on a distorted square by three N atoms of the ammine molecules and one O atom of the oxalate ligand. The crystal packing is stabilised by H bonds formed between ammine, water molecules and O atoms of oxalate. The complex underwent thermal decomposition at 200–231°C in  $\text{N}_2$  atmosphere, giving rise to Pt,  $\text{NH}_3$  and  $\text{CO}_2$ .

## MEDICAL AND DENTAL

### Mechanism of Unique Hardening of Dental Ag–Pd–Au–Cu Alloys in Relation with Constitutional Phases

Y. Kim, M. Niinomi, M. Nakai, T. Akahori, T. Kanno and H. Fukui, *J. Alloys Compd.*, 2012, **519**, 15–24

A commercial dental Ag–Pd–Au–Cu alloy (Ishifuku Metal Industry Co, Ltd, Tokyo, Japan) fabricated by cold rolling consisted of Cu-rich  $\alpha_1$ , Ag-rich  $\alpha_2$  and  $\beta$  phases. Ag–Pd–Au–Cu alloy fabricated by the liquid rapid solidification (LRS) method consisted of single  $\alpha$  phase. Both alloys were subjected to various heat treatments. In the alloy fabricated by cold rolling, the fine  $\text{L1}_0$ -type-ordered  $\beta'$  phase is precipitated and the coarse  $\beta$  phase is remained after solution treatment at 1123 K. The hardness increases drastically. In the alloy fabricated by LRS, the single  $\alpha$  phase was decomposed into the  $\alpha_1$  phase and the  $\alpha_2$  phase after solution treatment at 1023 K and its hardness change was small. However, after ageing treatment at 673 K, the fine  $\beta$  phase is precipitated in the  $\alpha$  phase and the hardness increases greatly even in the alloy fabricated by the LRS method.

## NANOTECHNOLOGY

### Enhanced Thermal Stability of Au@Pt Nanoparticles by Tuning Shell Thickness: Insights from Atomistic Simulations

Y.-H. Wen, R. Huang, C. Li, Z.-Z. Zhu and S.-G. Sun, *J. Mater. Chem.*, 2012, **22**, (15), 7380–7386

Molecular dynamics simulations were used to investigate the thermal stabilities of  $\text{Au}_{\text{core}}/\text{Pt}_{\text{shell}}$  bimetallic NPs. The thermal stabilities of core-shell NPs are significantly enhanced with increasing thickness of the Pt shell. When the core size or shell thickness is very small, the melting is initiated in the shell and gradually spreads into the core. As the core increases up to moderate size, an inhomogeneous melting was observed. Due to the relatively weak confinement of the thin shell, local lattice instability preferentially takes place in the core, leading to the inhomogeneous premelting of the Au core ahead of the overall melting of the Pt shell.

## PHOTOCONVERSION

### Evaluation of a Ruthenium Oxyquinolate Architecture for Dye-Sensitized Solar Cells

H. C. Zhao, J. P. Harney, Y.-T. Huang, J.-H. Yum, Md. K. Nazeeruddin, M. Grätzel, M.-K. Tsai and J. Rochford, *Inorg. Chem.*, 2012, **51**, (1), 1–3

$[\text{Ru}(\text{dcbpy})_2(\text{OQN})]^+$  (dcbpy = 4,4'-dicarboxy-2,2'-bipyridyl;  $\text{OQN}^-$  = 8-oxyquinolate) was prepared. Spectroscopic, electrochemical and theoretical analyses are indicative of extensive Ru d( $\pi$ ) molecular orbital overlap due to degenerate Ru d( $\pi$ ) and OQN p( $\pi$ ) mixing.  $[\text{Ru}(\text{dcbpy})_2(\text{OQN})]^+$  exhibited spectroscopic properties similar to those of the N3 dye. Its solar power conversion efficiency will require further optimisation.

## SURFACE COATINGS

### Research Situation of Precursors for Palladium Thin Films by MOCVD Process

G. Chen, Q. Chang, X. Chen, Q. Ye, L. Chen and W. Liu, *Precious Met. (Chin.)*, 2012, **33**, (1), 78–83

Pd thin films have wide application as protective coating for high temperature, dielectric films in microelectronics and catalysis. Advances in the preparation of Pd films by metal organic chemical vapor deposition are reviewed. The advantages and disadvantages of various precursors such as  $\text{Pd}(\eta^3\text{-ally})_2$ ,  $\text{Pd}(\text{acac})_2$  and  $\text{Pd}(\text{Me})_2(\text{PMe}_3)_2$  are discussed. (Contains 19 references.)

### Atomic Layer Deposition of Osmium

J. Hämäläinen, T. Sajavaara, E. Puukilainen, M. Ritala and M. Leskelä, *Chem. Mater.*, 2012, **24**, (1), 55–60

Os thin films and NPs were grown using atomic layer deposition. The Os thin films were successfully grown between 325°C and 375°C using osmocene ( $\text{OsCp}_2$ ) and molecular  $\text{O}_2$ . The films consisted of only Os

metal. The impurity contents of O, C and H were less than 1 at% each at all deposition temperatures. The deposition process has a substantial nucleation delay of ~350 cycles at 350°C on the  $\text{Al}_2\text{O}_3$  surface, which means that either NPs or thin films can be easily deposited by adjusting the number of deposition cycles.

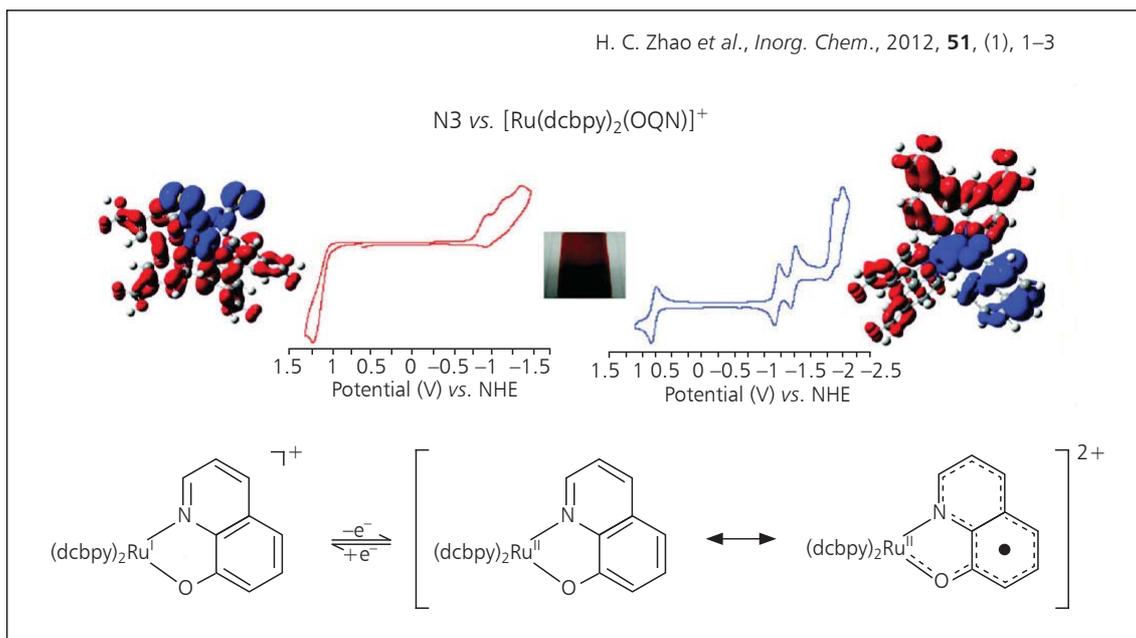


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