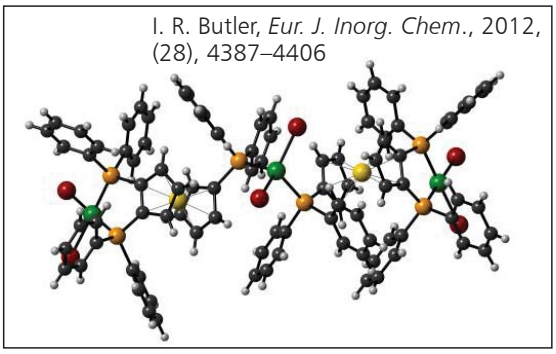
Abstracts

CATALYSIS – APPLIED AND PHYSICAL ASPECTS

The Simple Synthesis of Ferrocene Ligands from a Practitioner's Perspective

I. R. Butler, *Eur. J. Inorg. Chem.*, 2012, (28), 4387–4406

This is a review on the synthesis of ferrocene-based ligands, including chiral ligands, which have been prepared for use in catalysis principally using Ni, Pd, Ru, Rh and Pt metals. A number of ligand classes are reviewed including multidentate ferrocenylphosphanes used in the preparation of multimetallic Pd complexes. These are discussed in terms of catalytic applications and the rationale for the synthetic design. Relevant catalytic applications discussed range from coupling reactions to methoxycarbonylation. A range of highly basic ligands are also described which offer new reactivity in their metal complexes. (Contains 212 references.)



Pd@Aluminium Foil: a Highly Efficient and Environment-Friendly "Tea Bag" Style Catalyst with High TON

L. Fan, R. Yi, L. Yu, Y. Wu, T. Chen and R. Guo, *Catal. Sci. Technol.*, 2012, **2**, (6), 1136–1139

A novel 'tea bag' style catalyst, Pd@Al foil, was prepared by heating Al foil (area 1 cm × 1 cm) in a xylene solution of $Pd(OAc)_2$. The Pd coated Al foil catalysed the Suzuki-Miyaura cross-coupling reaction under mild conditions and the yield was extremely high. When a 10-times scale (5 mmol) reaction was catalysed by one piece of Pd@Al foil, diphenyl was obtained in 93% yield. This catalyst was easily separated after reaction and could be reused many times.

CATALYSIS – INDUSTRIAL PROCESS

Asymmetric Homogeneous Hydrogenations at Scale

D. J. Ager, A. H. M. de Vries and J. G. de Vries, *Chem. Soc. Rev.*, 2012, **41**, (8), 3340–3380

Asymmetric hydrogenations have been carried out at scale by a wide range of companies as a way to introduce stereogenic centres to commercially important molecules. The use of robotics and parallel reactions make finding a suitable catalyst much faster. As the new stereogenic centre is made as a single isomer, there is no waste from this approach. Commercial use levels of the pgm catalysts mean that the cost contribution to the product is relatively low. The metal waste can also be recycled at the end of the reaction. Overall the approach provides a cost effective route to many compounds. (Contains 353 references.)

CATALYSIS – REACTIONS

Formation of Acetals under Rhodium-Catalyzed Hydroformylation Conditions in Alcohols

O. Diebolt, C. Cruzeuil, C. Müller and D. Vogt, *Adv. Synth. Catal.*, 2012, **354**, (4), 670–677

Rh-catalysed hydroformylation of terminal alkenes with alcohols as solvents gave rise to the selective formation of the corresponding acetals. Using the Xantphos ligand achieved the best results with acetal selectivities >99% and linear/branched ratios of up to 52. Acetals were unreactive under hydroaminomethylation conditions.

Rh-Based Biphasic Isomerization of Carbon–Carbon Double Bonds in Natural Oils

R. L. Quirino and R. C. Larock, *J. Am. Oil Chem. Soc.*, 2012, **89**, (6), 1113–1124

The biphasic conjugation of natural oils such as soybean, as well as the isomerisation of various alkenes, was investigated using a Rh catalyst. The highest yield of conjugated soybean oil (96%) was obtained at 80ºC under Ar with EtOH as the polar solvent, using triphenylphosphine monosulfonate sodium salt (tppms) as the ligand and sodium dodecyl sulfate as the surfactant.

EMISSIONS CONTROL

Improved Palladium Only Three-Way Catalysts Using Phosphorus Modified Alumina Support

M. Shen, L. Song, J. Wang and X. Wang, *Catal. Commun.*, 2012, **22**, 28–33

Alumina support samples with different amounts of P dopants were prepared by the sol–gel method. The P-doped samples gave improved catalytic activity for CO/NOx/HC conversion. Moderate improvements of Pd dispersion were also seen in these samples. The surface area of γ-alumina increased with increasing amounts of P dopant and P was found to hinder the phase transition of γ-alumina at high temperatures. Aged P-doped catalysts exhibited outstanding TWC activities. The P–O–Al sites strongly inhibited Pd sintering during hydrothermal treatment.

FUEL CELLS

Electro-oxidation of CO_{chem} on Pt Nanosurfaces: Solution of the Peak Multiplicity Puzzle

P. Urchaga, S. Baranton, C. Coutanceau and G. Jerkiewicz, *Langmuir*, 2012, **28**, (7), 3658–3663

Oxidative stripping voltammograms were obtained for CO_{chem} preadsorbed on cubic, octahedral and cuboctahedral Pt NPs with preferentially oriented and atomically flat domains. They were compared to those for etched and thermally treated Pt(poly) electrodes with atomically flat, ordered surface domains separated by grain boundaries as well as those for spherical Pt NPs. The CO_{chem} oxidative stripping voltammograms consisted of up to four features that could be assigned to surface domains that are either preferentially oriented or disordered. The chemisorption and stripping of CO did not modify Pt NPs which preserved their shape and surface orientation.

Pd/Co Bimetallic Nanoparticles: Coelectrodeposition under Protection of PVP and Enhanced Electrocatalytic Activity for Ethanol Electrooxidation

Z.-S. Yang and J.-J. Wu, *Fuel Cells*, 2012, **12**, (3), 420–425

Pd-Co bimetallic nanostructures with Co compositions ranging from 0–13 at% were fabricated on glassy carbon electrodes by one-step electrodeposition in the presence of PVP. PVP was used as an additive to stabilise the Pd NPs and inhibit agglomeration during their formation. $Pd_{100}Co_{10}$ exhibited high catalytic activity towards EtOH oxidation in alkaline media.

ELECTRICAL AND ELECTRONICS

Fluid-Kinetics Enhanced Selective Etching Process of NiPt Film by Piranha Chemistry in Silicide Formation for Complementary Metal Oxide Semiconductor Fabrication

M. M. Chu and J.-H. Chou, *Thin Solid Films*, 2012, **520**, (16), 5482–5488

NiPtSi has potential for the CMOS self-aligned silicidation process beyond the 22 nm node. Fresh H_2SO_4 based piranha chemistry at >150ºC can etch Pt with less damage to the exposed wafer surface. By using a larger mass-to-charge density Pt redox reaction zone, stronger chemical fluid kinetics and intensified voltammetric cycles, the Pt selective removal rate can be increased. Two types of wet chemical processors were used to examine the effect of fluid-chemical kinetics on the selective etching rate of Pt.

MEDICAL AND DENTAL

Crossed-Wire Laser Microwelding of Pt-10 Pct Ir to 316 Low-Carbon Vacuum Melted Stainless Steel: Part I. Mechanism of Joint Formation

G. S. Zou, Y. D. Huang, A. Pequegnat, X. G. Li, M. I. Khan and Y. Zhou, *Metall. Mater. Trans. A*, 2012, **43**, (4), 1223–1233

With the increasing complexity of medical devices, the challenge of joining dissimilar materials arises. Laser microwelding of Pt-10% Ir to 316 low C vacuum melted (LVM) stainless steel (SS) crossed wires was undertaken. The mechanisms of joint formation transitioned from brazing to a combination of brazing and fusion welding, and then to fusion welding with increasing pulsed laser energy. The joints exhibited various tensile failure modes. The optimal laser peak power range to produce joints with good joint geometry and 90% of the tensile strength of the Pt-10% Ir wire was found.

Crossed-Wire Laser Microwelding of Pt-10 Pct Ir to 316 LVM Stainless Steel: Part II. Effect of Orientation on Joining Mechanism

Y. D. Huang, A. Pequegnat, G. S. Zou, J. C. Feng, M. I. Khan and Y. Zhou, *Metall. Mater. Trans. A*, 2012, **43**, (4), 1234–1243

The laser weldability of joints between Pt-10% Ir and 316 LVM SS crossed wires was evaluated to determine the effect of orientation of the two dissimilar metals (i.e. which metal was exposed to the laser beam) on weld quality. With the Pt-Ir alloy on top, a significant amount of porosity was present on the surface of the welds as well as throughout the weld cross-sections.

This porosity is proposed to be a result of preferential vapourisation of 316 LVM SS alloying elements that become mixed with the molten Pt-10% Ir.

NANOTECHNOLOGY

Formation of Porous Pt Nanoparticles through Core–Shell Pt–Al Nanoalloys and Wet Chemical Etching

Z. Shen, Y. Matsuki, K. Higashimine, M. Miyake and T. Shimoda, *Chem. Lett.*, 2012, **41**, (6), 644–646

A core–shell PtAl nanoalloy was prepared by selective deposition of Al on a Pt nanocube and wet chemical etching was carried out on the PtAl nanoalloy to produce a porous Pt NP. The Pt nanocube serves as a catalyst for dehydrogenation of alane (AlH_3) and as the seed for Al crystallisation. During the formation of the Al shell, Pt atoms diffuse into the Al layer to form a core–shell structure of a PtAl nanoalloy surrounding a Pt core. The chemical etching process produces porous Pt NPs with high catalytic activity.

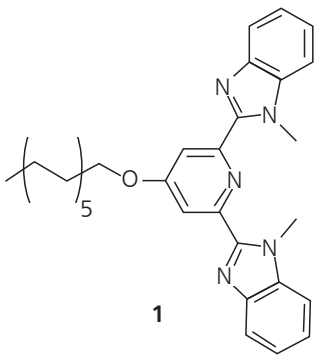
PHOTOCONVERSION

Vapochromic and Mechanochromic Films from Square-Planar Platinum Complexes in Polymethacrylates

J. R. Kumpfer, S. D. Taylor, W. B. Connick and S. J. Rowan, *J. Mater. Chem.*, 2012, **22**, (28), 14196–14204

Square-planar [Pt(**1**)Cl](PF$_6$) (**1** = 4-dodecyloxy-2,6-bis(*N*-methylbenzimidazol-2′-yl)pyridine) was blended into a series of methacrylate polymers. The polymer films displayed vapochromic (yellow to red) and vapoluminescent behaviour after exposure to MeCN liquid or vapour, as a result of a vapour induced change in the Pt–Pt interactions. The rate of recovery of the yellow colour was found to be dependent on the T_g of the matrices. The polymer–Pt complex blends also displayed mechanochromic and mechanoluminescent properties upon deformation by compression, scratching or stretching.

J. R. Kumpfer *et al.*, *J. Mater. Chem.*, 2012, **22**, (28), 14196–14204



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Simple Novel Cyclometallated Iridium Complexes for Potential Application in Dye-Sensitized Solar Cells

C. Dragonetti, A. Valore, A. Colombo, S. Righetto and V. Trifiletti, *Inorg. Chim. Acta*, 2012, **388**, 163–167

Ir complexes are potentially good candidates for application in DSSCs. Three simple cyclometallated Ir(III) complexes of the type: [Ir(C^N)$_2$(4,4′-dicarboxybipyridine)][PF$_6$] (C^N = variously substituted phenylpyridine cyclometallating ligands) were synthesised and the influence of the ligand on photovoltaic performance was assessed. More conjugated π-delocalised cyclometallating ligands that slightly shift the UV bands to higher wavelengths gave slightly better photovoltaic parameters.

SURFACE COATINGS

Thermal Decomposition and Fractal Properties of Sputter-Deposited Platinum Oxide Thin Films

A. Mosquera, D. Horwat, L. Vazquez, A. Gutiérrez, A. Erko, A. Anders, J. Andersson and J. L. Endrino, *J. Mater. Res.*, 2012, **27**, (5), 829–836

Porous Pt thin films were obtained by thermal decomposition of Pt oxide films at temperatures between 25–675ºC. The decomposition of the oxide began at 400ºC and followed a sigmoidal trend with increasing annealing temperature. In XRD spectra, only an amorphous-like signature was observed at <575ºC, while Pt 4f XPS showed that the deposited oxide was a mixture of PtO_2 and PtO. Pt-L_3 edge XANES and Pt 4f XPS spectra showed that the Pt concentration and electronic structure were predominant at ≥575ºC.

Synthesis of B2-RuAl Coatings on Mild Steel by Laser Cladding

B. Bax, C. Pauly, P. Leibenguth, K. Woll and F. Mücklich, *Surf. Coat. Technol.*, 2012, **206**, (19–20), 3931–3937

Powder mixtures of Ru and Al were laser clad on mild steel using a 500 W diode laser. The quality of the coatings was dependent on the parameters used. The coatings were found to be a mixture of B2-RuAl with a high amount of Fe as a substitutional element plus α-Fe. When superimposing several layers, the fraction of α-phase in the top layer decreased significantly with each additional layer. This method has potential for coating structures for high-temperature applications.