

ABSTRACTS

CATALYSIS – APPLIED AND PHYSICAL ASPECTS

Toward Less Dependence on Platinum Group

Metal Catalysts: The Merits of Utilizing Tin

R. D. ADAMS, D. A. BLOM, B. CAPTAIN, R. RAJA, J. M. THOMAS and E. TRUFAN, *Langmuir*, 2008, 24, (17), 9223–9226

Minute stoichiometric bimetallic clusters rich in Sn (PtSn₂, RhSn₂, RuSn₂) were shown to be powerful selective hydrogenation catalysts. These “molecular metallic” entities were supported on mesoporous SiO₂. High percentages of cyclododecene were obtained at fractional conversions ranging from 0.45–0.70 of the parent 1,5,9-cyclododecatriene at T = 373 K and under solvent-free conditions.

Selective Oxidation of Glucose to Gluconic Acid over Argon Plasma Reduced Pd/Al₂O₃

X. LIANG, C.-J. LIU and P. KUAI, *Green Chem.*, 2008, 10, (12), 1318–1322

An Ar glow discharge plasma approach was used to reduce PdCl₂ supported on γ -Al₂O₃ at room temperature. The catalyst formed using plasma reduction followed by calcination under Ar at 500°C exhibited a higher activity for selective oxidation of glucose than a H₂ thermally reduced catalyst. The plasma reduced catalysts possessed high stability against leaching of active metal into the reaction medium.

Vapor-Phase Selective Hydrogenation of Citral over Pd/Bentonite: Effect of Reduction Method

D. DIVAKAR, D. MANIKANDAN and T. SIVAKUMAR, *J. Chem. Technol. Biotechnol.*, 2008, 83, (11), 1472–1478

Well-dispersed Pd nanoparticles were prepared by a wet impregnation technique over bentonite followed by reduction with H₂, NaBH₄ or EtOH. Hydrogenation of citral over Pd/bentonite was studied in the vapour phase using a microreactor. Pd/bentonite reduced by EtOH was found to give the highest conversion and Pd/bentonite reduced by NaBH₄ was found to give the highest selectivity towards nerol and geraniol. This was attributed to the smallest particle size of Pd in the former catalyst and the presence of B species on the latter catalyst, respectively.

One-Pot Rapid Low-Cost Synthesis of Pd-Fullerite Catalysts

L. C. CHONG, V. STOLOJAN, G. WAGNER, S. R. P. SILVA and R. J. CURRY, *J. Mater. Chem.*, 2008, 18, (40), 4808–4813

Tetrakis(triphenylphosphine)palladium (1) was used as a precursor for the deposition of Pd clusters upon a fullerite during growth using a rapid liquid/liquid interface precipitation. Variation of the ratio of (1) to C₆₀ was used to control the aspect ratio of the nanostructures. The presence of (η^2 -C₆₀)Pd(PPh₃)₂ and highly dispersed Pd clusters on the fullerites was established. Pd-fullerite was active as a catalyst for the hydrogenation of 1-ethynyl-1-cyclohexanol under H₂.

CATALYSIS – REACTIONS

Rhodium(III) and Iridium(III) Complexes with Quinolylyl-Functionalized Cp Ligands: Synthesis and Catalytic Hydrogenation Activity

G. KOHL, H. PRITZKOW and M. ENDERS, *Eur. J. Inorg. Chem.*, 2008, (27), 4230–4235

Bis(ethene) complexes of Rh(I) and Ir(I) with 8-quinolylylcyclopentadienyl ligands (Cp^Q and Cp^{Q*}) were oxidised photochemically with Cl-containing solvents or by I₂. Upon oxidation, the quinoline ring rotates and the N donor coordinates to the metal centres. Substitution of the halogenido ligands through acetato groups gave highly soluble derivatives, in which the acetate moiety acts as a monodentate or bidentate ligand. The resulting Rh(III) complexes were used for the hydrogenation of 1-hexene. [Cp^QRh(O₂CCH₃)]⁺PF₆⁻ gave the highest activity.

Dihydroxylation of Olefins Catalyzed by Polystyrene-*sg*-imidazolium Resin-Supported Osmium Complex

B.-H. JUN, J.-H. KIM, J. PARK, H. KANG, S.-H. LEE and Y.-S. LEE, *Synlett*, 2008, (15), 2313–2316

OsO₄ was immobilised onto poly(1-methylimidazoliummethyl styrene)-surface grafted-PS resin. The formation of the Os complex occurred only on the surface of the polymer support. The catalyst exhibited excellent activity in the dihydroxylation of olefins and could be reused up to three times.

EMISSIONS CONTROL

On Board Catalytic NO_x Control: Mechanistic Aspects of the Regeneration of Lean NO_x Traps with H₂

P. FORZATTI, L. LIETTI and I. NOVA, *Energy Environ. Sci.*, 2008, 1, (2), 236–247

Mechanistic aspects of the reduction with H₂ of NO_x stored on lean NO_x trap Pt-Ba/Al₂O₃ catalysts are reviewed. Under nearly isothermal conditions, the first step is NH₃ formation through the reaction of H₂ with stored nitrates; in the second step, the NH₃ reacts with the nitrates left on the catalysts' surfaces leading to N₂ formation. The first step is much faster than the second. Both steps are catalysed by Pt.

Simultaneous Removal of Soot and NO_x over Ir-Based Catalysts in the Presence of Oxygen

R. ZHU, M. GUO and F. OUYANG, *Catal. Today*, 2008, 139, (1–2), 146–151

The TPR technique was used to study the simultaneous removal of soot and NO_x by Ir-based catalysts in the presence of O₂. A comparison between Ir/ γ -Al₂O₃ and Pt/ γ -Al₂O₃ demonstrated that the Ir catalyst was more effective. The 1 wt.% Ir/ZSM-5 catalyst exhibited a high level of activity for the simultaneous removal of soot and NO_x.

FUEL CELLS

Carbon Supported Pt–Pd Alloy as an Ethanol Tolerant Oxygen Reduction Electrocatalyst for Direct Ethanol Fuel Cells

T. LOPES, E. ANTOLINI and E. R. GONZALEZ, *Int. J. Hydrogen Energy*, 2008, 33, (20), 5563–5570

Pt–Pd/C (1) with a Pt:Pd atomic ratio 77:23 was prepared by reduction of metal precursors with formic acid. In EtOH-free H₂SO₄, (1) showed a slightly higher activity towards O₂ reduction compared to Pt. In the presence of EtOH a larger increase in overpotential of the ORR on Pt than on Pt–Pd was found, indicating a higher EtOH tolerance of (1).

Electrochemical Characteristics of Pd Anode Catalyst Modified with TiO₂ Nanoparticles in Polymer Electrolyte Fuel Cell

E. N. MUHAMAD, T. TAKEGUCHI, G. WANG, Y. ANZAI and W. UEDA, *J. Electrochem. Soc.*, 2009, 156, (1), B32–B37

The modification of a Pd/C catalyst with TiO₂ increased the activity for electrochemical oxidation of pure H₂, and gave high activity, similar to that of a Pt/C catalyst. The TiO₂ increased the dispersion of Pd particles, which resulted in an increase in the active surface area of the catalyst. The effect of TiO₂ addition on the performance of a fuel cell with a Pd anode in a 500 ppm CO-contaminated H₂ fuel was investigated. The Pd/TiO₂/C catalyst had a higher CO tolerance than Pt/C for maintaining high activity for electrochemical oxidation of H₂.

METALLURGY AND MATERIALS

Exfoliated Graphene Separated by Platinum Nanoparticles

Y. SI and E. T. SAMULSKI, *Chem. Mater.*, 2008, 20, (21), 6792–6797

A mechanically exfoliated, high-surface area Pt nanoparticle–graphene composite was obtained by drying aqueous dispersions of Pt nanoparticles adhered to graphene. Pt nanoparticles were fixed to graphene by reduction of H₂PtCl₆ with MeOH in the presence of 3-(N,N-dimethyldodecylammonio) propanesulfonate. The Pt nanoparticles act as spacers.

Microstructural and Magnetic Properties of CoPt Nanowires

H. KHURSHID, Y. H. HUANG, M. J. BONDER and G. C. HADJIPANAYIS, *J. Magn. Magn. Mater.*, 2009, 321, (4), 277–280

CoPt nanowires (1) of high aspect ratio were prepared by electrodeposition into anodised alumina templates using electrolyte at pH 2–6. The as-made (1) exhibit an f.c.c. structure with soft magnetic properties which transform into the f.c.t. L1₀ phase after thermal treatment. (1) prepared at high pH were f.c.c. nanorods. Thermal annealing led to a preferred (0 0 1) orientation. (1) prepared at lower pH were f.c.c. nanograins. Magnetisation curves for the latter sample were virtually identical in both directions.

Analysis of Deuterium Permeation through Pd₈₁Pt₁₉ Alloy at Stress Conditions

D. DUDEK, *Pol. J. Chem.*, 2008, 82, (10), 1941–1947

The permeation of D₂ through a Pd₈₁Pt₁₉ alloy membrane (1) under stress conditions was examined at constant temperature $T = 278.2$ K and pressures up to 900 hPa(D₂). The permeation curves were determined at different initial and boundary conditions. The D₂ fluxes were calculated by fitting experimental points with straight lines in the stationary parts of the permeation curves. The D₂ permeation through (1) was shown to be changed by stresses created during metal lattice expansion processes.

Synthesis of Nanosized Zn₂PtO₄

P. KJELLIN and A. E. C. PALMQVIST, *J. Mater. Sci.*, 2008, 43, (22), 7250–7253

A new facile metathetical preparation of nanosized Zn₂PtO₄ uses PtCl₄ mixed with ZnO nanopowder. Relatively low temperature (500°C) and ambient pressure can be employed. The product is washed with HCl in order to remove unreacted ZnO and formed ZnCl₂. The small particle size of the Zn₂PtO₄ makes it suitable for use in catalyst preparation.

Thermochemistry of Pd–In, Pd–Sn and Pd–Zn Alloy Systems

S. AMORE, S. DELSANTE, N. PARODI and G. BORZONE, *Thermochim. Acta*, 2009, 481, (1–2), 1–6

A high-temperature direct drop calorimeter was used to study the standard enthalpies of formation of solid Pd–M (M = In, Sn and Zn) alloys at 300 K in the M-rich region. The values of ΔH_f (kJ mol⁻¹ atoms⁻¹) for the following phases were obtained: PdIn (49 at.% In): -69.0 ± 1.0 ; Pd₂In₃ (-57.0 ± 1.0); Pd₃In₇: -43.0 ± 1.0 ; PdSn₂: -50.0 ± 1.0 ; Pd₂Zn₉ (77 at.% Zn): -33.7 ± 1.0 ; Pd₂Zn₉ (78 at.% Zn): -34.0 ± 1.0 ; Pd₂Zn₉ (80 at.% Zn): -35.0 ± 1.0 . The obtained results show exothermic values which increase from Pd–Zn to Pd–Sn and Pd–In.

APPARATUS AND TECHNIQUE

A Simple Colorimetric Luminescent Oxygen Sensor Using a Green LED with Pt Octaethylporphyrin in Ethyl Cellulose as the Oxygen-Responsive Element

S. R. RICKETTS and P. DOUGLAS, *Sens. Actuators B: Chem.*, 2008, 135, (1), 46–51

A green LED, in an O₂ sensor (1), acts as both a green emission source and an excitation source for a film of O₂-sensitive Pt octaethylporphyrin in ethyl cellulose containing TiO₂ or ZnO as a scattering agent. (1) has a “traffic light”, red–yellow–green, response to increasing O₂ concentration. Singlet O₂ stabiliser diazobicyclo[2.2.2]octane increased the stability of (1) significantly. Because of the relatively thick sensor layer used in (1), response times are long, with 90% response times of ~ 1000 s for N₂ to O₂ and ~ 300 s for O₂ to N₂.

CHEMISTRY

Synthesis of a Platinum(II) Bis(trimethylsilyl)amido Complex: A Better Starting Material for the Cyclometalation of Pincer Ligands

A. ARUNACHALAMPILLAI, M. T. JOHNSON and O. F. WENDT, *Organometallics*, 2008, 27, (17), 4541–4543

Treatment of $[(\text{COD})\text{PtCl}_2]$ with $\text{LiN}(\text{SiMe}_3)_2$ in ether at room temperature gave $[\text{COD}]\text{PtClN}(\text{SiMe}_3)_2$ (1). The X-ray structure of (1) shows the expected mononuclear pseudo-square-planar Pt in which the chlorine and amido groups are *cis* to each other. (1) was shown to be a convenient starting material for the preparation of PXP Pt pincer complexes.

An Unprecedented Bonding Mode for Potassium within a PCP-Pincer Palladium Hydride-K-Selectride® Complex

B. J. BORO, E. N. DUESLER, K. I. GOLDBERG and R. A. KEMP, *Inorg. Chem. Commun.*, 2008, 11, (12), 1426–1429

The reaction of $(\text{PCP})^i\text{PdCl}$ and the reductant K-Selectride® solution ($\text{K}(\text{sec-Bu}_3\text{BH})$) in THF did not yield a simple $(\text{PCP})^i\text{PdH}$ species; an adduct (1) that contains bound $\text{K}(\text{sec-Bu}_3\text{BH})$ was obtained. (1) was shown to be a centrosymmetric dimer in the solid state by X-ray crystallography. The tri-coordinate K^+ ion bonds only to the terminal Pd hydride and the two bridging B hydrides.

Competitive C–I versus C–CN Reductive Elimination from a Rh^{III} Complex. Selectivity is Controlled by the Solvent

M. FELLER, M. A. IRON, L. J. W. SHIMON, Y. DISKIN-POSNER, G. LEITUS and D. MILSTEIN, *J. Am. Chem. Soc.*, 2008, 130, (44), 14374–14375

The oxidative addition of MeI to $[(\text{PNP})\text{Rh}(\text{CN})]$ (1) gave $[(\text{PNP})\text{Rh}(\text{CN})(\text{CH}_3)][\text{I}]$ (2). (2) reacts selectively in two pathways. In aprotic solvents C–I reductive elimination of MeI followed by its electrophilic attack on the cyano ligand takes place, giving $[(\text{PNP})\text{Rh}(\text{CNCH}_3)][\text{I}]$, while in protic solvents C–C reductive elimination of MeCN takes place forming $[(\text{PNP})\text{RhI}]$. Reaction of (1) with EtI in aprotic solvents gave the corresponding isonitrile complex.

ELECTRICAL AND ELECTRONICS

Thermally-Treated Pt-Coated Silicon AFM Tips for Wear Resistance in Ferroelectric Data Storage

B. BHUSHAN, M. PALACIO and K. J. KWAK, *Acta Mater.*, 2008, 56, (16), 4233–4241

A commercial Pt-coated Si AFM probe was thermally treated in order to form Pt silicide at the near-surface. Nanoindentation, nanoscratch and wear experiments evaluated the mechanical properties and wear performance at high velocities. The thermally treated tip exhibited lower wear than the untreated tip. The enhancement in mechanical properties and wear resistance in the thermally treated film is attributed to silicide formation in the near-surface.

PHOTOCONVERSION

Conjugated Polymers Bearing Iridium Complexes for Triplet Photovoltaic Devices

G. L. SCHULZ and S. HOLDCROFT, *Chem. Mater.*, 2008, 20, (16), 5351–5355

Poly(9,9-dihexylfluorene-co-2-phenylpyridine) (1) and poly(9,9-dioctylfluorene-co-tris(2-phenylpyridine) iridium (III)) (2) were prepared using Suzuki polycondensation. An increase in per cent external quantum efficiency for (2) over (1), from 1.1 to 10.3, is attributed to the formation of the triplet state in (2), and by inference, longer diffusion lengths of the triplet exciton. Introducing the Ir complexes into the polyfluorene-based polymer blended with an electron acceptor enhanced solar cell conversion efficiencies.

On the Photophysical and Electrochemical Studies of Dye-Sensitized Solar Cells with the New Dye CYC-B1

J.-G. CHEN, C.-Y. CHEN, S.-J. WU, J.-Y. LI, C.-G. WU and K.-C. HO, *Sol. Energy Mater. Sol. Cells*, 2008, 92, (12), 1723–1727

The performance of nanocrystalline TiO_2 DSSC fabricated using CYC-B1 (Ru photosensitizer with an alkyl bithiophene group) dye-anchored TiO_2 photoelectrode showed an enhancement in cell efficiency when the TiO_2 film thickness was increased from 3 μm (eff. = 5.41%) to 6 μm (eff. = 7.19%). The efficiency was maximum at a film thickness of 6 μm , reached its limiting value and remained constant up to 53 μm . Although a similar trend was also observed for N3 dye, the maximum efficiency achieved was only at 27 μm thickness (eff. = 6.75%).

SURFACE COATINGS

Study of the Surface Morphology of Platinum Thin Films on Powdery Substrates Prepared by the Barrel Sputtering System

A. TAGUCHI, M. INOUE, C. HIROMI, M. TANIZAWA, T. KITAMI and T. ABE, *Vacuum*, 2008, 83, (3), 575–578

The transition of Pt from a nanoparticle to a film on SiO_2 particles was modified by using a sputtering system with a barrel-type powder sample holder. The morphology of Pt changed from highly dispersed nanoparticles to a worm-like structure followed by a continuous Pt film, depending on the amount of Pt modified. TEM showed that the Pt film in the worm-like structure had a uniform thickness of ~ 2.6 nm.

Study on Corrosion Resistance of Palladium Films on 316L Stainless Steel by Electroplating and Electroless Plating

J. TANG and Y. ZUO, *Corros. Sci.*, 2008, 50, (10), 2873–2878

Pd films with good adhesive strength were deposited on 316L stainless steel. The electroless plated Pd film (1) mainly consisted of Pd, P and N, and the electroplated Pd film (2) was almost pure Pd. Both plated samples showed corrosion resistance in strong corrosive media; (2) was slightly better than (1).