

ABSTRACTS

CATALYSIS – APPLIED AND PHYSICAL ASPECTS

Kinetics of *o*-Chlorotoluene Hydrogenolysis in the Presence of 3%, 5% and 10% Pd/C Catalysts

T. JANIÁK, *Appl. Catal. A: Gen.*, 2008, 335, (1), 7–14

The kinetics of *o*-chlorotoluene hydrogenolysis in the presence of 3%, 5% and 10% Pd/C (1) were studied in an alkaline-*n*-heptane-H₂(g) system. The main product of hydrogenolysis was toluene. The extent of dechlorination increased with time and temperature, and depended on the amount of (1).

Gas-Phase Thermochemistry of Ruthenium Carbene Metathesis Catalysts

S. TORKER, D. MERKI and P. CHEN, *J. Am. Chem. Soc.*, 2008, 130, (14), 4808–4814

Quantitative energy-resolved collision-induced dissociation cross-sections by tandem ESI-MS gave absolute thermochemical data for phosphine binding energies in first- and second-generation Ru metathesis catalysts of 33.4 and 36.9 kcal mol⁻¹, respectively. A study of RCM in the second-generation system to liberate norbornene by forming the 14-electron reactive intermediate from the intramolecular π -complex allowed an estimate of the olefin binding energy to the 14-electron complex of ~ 18 kcal mol⁻¹, assuming a loose transition state.

CATALYSIS – INDUSTRIAL PROCESS

Development of a Robust Ring-Closing Metathesis Reaction in the Synthesis of SB-462795, a Cathepsin K Inhibitor

H. WANG, S. N. GOODMAN, Q. DAI, G. W. STOCKDALE and W. M. CLARK, Jr., *Org. Process Res. Dev.*, 2008, 12, (2), 226–234

RCM with Hoveyda's second-generation catalyst can be used to synthesise SB-462795. With pure diene precursor (1), very low loadings (0.1–0.2 mol %) of the Ru catalyst are required; however, the reaction conversion decreased when (1) is of reduced purity. Projection methods were applied to historical data to identify the main sources of variation in starting material quality, and to determine the main detrimental impurities.

CATALYSIS – REACTIONS

Dendritic SBA-15 Supported Wilkinson's Catalyst for Hydroformylation of Styrene

P. LI and S. KAWI, *Catal. Today*, 2008, 131, (1–4), 61–69

PAMAM dendrimers were grown in mesoporous SBA-15. RhCl(PPh₃)₃ precursor was then tethered on these supports. The silanols outside the SBA-15 pores could be passivated. The Rh catalysts supported in the pore channels of this passivated SBA-15 showed positive dendritic effects in enhancing the catalytic activity, regioselectivity and stability of the catalyst by minimising the leaching of the Rh complex catalyst.

A Versatile Iridium Catalyst for Aldehyde Reduction in Water

X. WU, C. CORCORAN, S. YANG and J. XIAO, *ChemSusChem*, 2008, 1, (1–2), 71–74

Ir-*N*-tosyldiamine complexes catalysed the reduction of a wide range of aldehydes, including aromatic, aliphatic, heterocyclic and α,β -unsaturated aldehydes, in H₂O. The hydrogenations were fast and chemoselective. The reactions proceeded without the need for added organic cosolvents.

EMISSIONS CONTROL

Role of Zeolite Structure on NO Reduction with Diesel Fuel over Pt Supported Zeolite Catalysts

A. SULTANA, M. HANEDA, T. FUJITANI and H. HAMADA, *Microporous Mesoporous Mater.*, 2008, 111, (1–3), 488–492

The selective catalytic reduction of NO with diesel fuel over Pt/zeolites was investigated under simulated exhaust conditions. Pt/MOR was the most active, giving 90% NO conversion at 300°C, however Pt/FER showed a desirable low temperature window, giving 77% NO conversion at < 260°C. Over ZSM-5, BEA and Y with 3D pore structures, extensive carbonaceous deposits were observed. FER having a 1D pore structure did not allow extensive coke formation, resulting in low temperature NO conversion. It is suggested that NO reduction takes place mainly near the zeolite pore opening.

A New Route for Degradation of Volatile Organic Compounds under Visible Light: Using the Bifunctional Photocatalyst Pt/TiO_{2-x}N_x in H₂-O₂ Atmosphere

D. LI, Z. CHEN, Y. CHEN, W. LI, H. HUANG, Y. HE and X. FU, *Environ. Sci. Technol.*, 2008, 42, (6), 2130–2135

N-doped and Pt-modified TiO₂ was used to obtain Pt/TiO_{2-x}N_x (1) by wet impregnation of TiO₂ xerogel. Superior photocatalytic activity and catalytic stability of (1) for decomposing benzene were achieved under visible light in a H₂-O₂ atmosphere. (1) also successfully decomposed other VOCs such as toluene, ethylbenzene, cyclohexane and acetone.

Modification of Pd/Al₂O₃ Catalyst to Improve the Catalytic Reduction of NO in Waste Incineration Processes

J. C. CHEN, F. Y. CHANG and M. Y. WEY, *Catal. Commun.*, 2008, 9, (6), 1106–1110

Na, Cu, Ni and Co were used to modify Pd/Al₂O₃ catalysts (1) for NO reduction with CO reductant in a simulated flue gas containing 6% O₂. Na addition was very effective in promoting the NO conversion of (1) at 300–400°C with the concentration ratio of CO:NO = 1. Adding Cu improved the NO conversion at 250–300°C. Ni or Co slightly improved the NO conversion at 150°C, but maintained good catalytic activity on the CO oxidation.

FUEL CELLS

Crystallographic Characteristics of Nanostructured Thin-Film Fuel Cell Electrocatalysts: A HRTEM Study

L. GANCS, T. KOBAYASHI, M. K. DEBE, R. ATANASOSKI and A. WIECKOWSKI, *Chem. Mater.*, 2008, 20, (7), 2444–2454

The structure of nanostructured thin film (NSTF) electrocatalysts supported on PR149 (*N,N*-di(3,5-xylyl)perylene-3,4,9,10-bis(dicarboximide))-crystalline organic whiskers was investigated by HTREM. Common trends in the electrocatalyst crystallography, morphology and surface characteristics were observed for Pt, PtRu and PtNiFe NSTFs. Specific details of the electrocatalyst particles' growth mechanisms, morphology and support interactions were established.

A High-Throughput Study of PtNiZr Catalysts for Application in PEM Fuel Cells

J. F. WHITACRE, T. I. VALDEZ and S. R. NARAYANAN, *Electrochim. Acta*, 2008, 53, (10), 3680–3689

Pure Pt or PtNiZr alloys (not exceeding 11 at.% Zr) were fabricated using cosputter deposition. A high-throughput fabrication approach was used wherein 18 thin film ORR electrocatalyst alloy samples were deposited onto a large-area substrate. A multichannel pseudo-potentiostat enabled the simultaneous quantitative study of catalytic activity for all of the electrodes in a single test bath. The best performing catalyst was Pt₅₀Ni₃₀Zr₂.

In Situ and Real-Time Visualisation of Oxygen Distribution in DMFC Using a Porphyrin Dye Compound

J. INUKAI, K. MIYATAKE, Y. ISHIGAMI, M. WATANABE, T. HYAKUTAKE, H. NISHIDE, Y. NAGUMO, M. WATANABE and A. TANAKA, *Chem. Commun.*, 2008, (15), 1750–1752

A film of the luminescent dye [tetrakis(pentafluorophenyl)porphyrinato]platinum dispersed in poly(1-trimethylsilyl-1-propyne) was coated onto a transparent separator on the cathode side of a DMFC to visualise O distribution under operating conditions by analysing emission from the dye. Higher O consumption due to MeOH crossover occurred for a fluorinated membrane than for a hydrocarbon membrane.

Improved Performance of Pd Electrocatalyst Supported on Ultrahigh Surface Area Hollow Carbon Spheres for Direct Alcohol Fuel Cells

F. P. HU, Z. WANG, Y. LI, C. LI, X. ZHANG and P. K. SHEN, *J. Power Sources*, 2008, 177, (1), 61–66

Hollow C spheres (HCSs) were prepared using glucose as the C source and polystyrene spheres as the template. Combined methods of hydrothermal and intermittent microwave heating were employed. The addition of PEG-block-PPG-block-PEG during the hydrothermal process greatly increased the surface area of the HCS, mainly from the huge micropores. The catalytic activity of Pd/HCSs is 3 times higher than Pd/Vulcan XC-72 C at the same Pd loadings.

METALLURGY AND MATERIALS

Hydrogen Absorption in the Core/Shell Interface of Pd/Pt Nanoparticles

H. KOBAYASHI, M. YAMAUCHI, H. KITAGAWA, Y. KUBOTA, K. KATO and M. TAKATA, *J. Am. Chem. Soc.*, 2008, 130, (6), 1818–1819

From the results of H₂ pressure-composition isotherm and solid-state ²H NMR measurements, it was shown that Pd/Pt bimetallic nanoparticles (1) with a Pd core/Pt shell structure can absorb H₂. Most of the absorbed H atoms were situated around the interfacial region between the Pd core and the Pt shell. This indicates that the core/shell boundary plays a key role in the formation of the hydride phase of (1).

Hydrogen Storage Properties of Pd Nanoparticle/Carbon Template Composites

R. CAMPESI, F. CUEVAS, R. GADIOU, E. LEROY, M. HIRSCHER, C. VIX-GUTERL and M. LATROCHE, *Carbon*, 2008, 46, (2), 206–214

A C/Pd composite was prepared by chemical impregnation of an ordered porous C template (CT) with a H₂PdCl₄ solution followed by a reduction treatment. 10 wt.% of Pd clusters (2 nm in size) were introduced in the C porosity. At room temperature and moderate pressure (0.5 MPa), the filling of the CT with nanocrystalline Pd resulted in an H₂ uptake eight times larger than that of the Pd-free CT.

APPARATUS AND TECHNIQUE

Gas Sensing Properties of Nano SnO₂ Based Thick Films Prepared by Dip Coating Method with Effect of Molarity of PtCl₂ Solution

A. D. GARJE and R. C. AIYER, *J. Mater. Sci.: Mater. Electron.*, 2008, 19, (6), 547–552

The title films modified by dip coating in PtCl₂ solutions (0.05–0.2 M) were tested for 400 ppm concentration of H₂, CO and LPG. Sensors dip coated with 0.15 M solution of PtCl₂ showed the highest sensitivity which is ten times higher than undoped SnO₂ sensors. The sensors have fast response time of 10 s to all the gases with a minimum detection limit of 10 ppm.

Micro Coulter Counters with Platinum Black Electroplated Electrodes for Human Blood Cell Sensing

S. ZHENG, M. LIU and Y.-C. TAI, *Biomed. Microdevices*, 2008, 10, (2), 221–231

Two designs of micro Coulter counter were fabricated using integrated parylene and soft lithography technologies. Pt black enhanced detection in the intermediate frequency range (~ 100 Hz to 7 MHz). Polystyrene beads were used to validate the operation of the devices, and using excitation frequency of 10 kHz, the signal magnitude was found to be correlated with the volume of the individual bead. Human blood cell sensing was then demonstrated with diluted whole blood and leukocyte rich plasma under the same excitation frequency.

CHEMISTRY

Structure of a Crystalline Vapochromic Platinum(II) Salt

L. J. GROVE, A. G. OLIVER, J. A. KRAUSE and W. B. CONNICK, *Inorg. Chem.*, 2008, 47, (5), 1408–1410

Square-planar cations of the orange form of [Pt(Me₂bzimpy)Cl](PF₆)·DMF (Me₂bzimpy = 2,6-bis(*N*-methylbenzimidazol-2-yl)pyridine) stack along the *b* axis in a head-to-tail arrangement with short interplanar spacings (3.35 and 3.39 Å). The DMF solvent molecules line channels parallel to *c*, which may provide a channel for vapour absorption. Crystals were shown to be vapochromic, changing from orange to violet upon exposure to MeCN vapour.

Synthesis and Dynamic Structure of Multinuclear Rh Complexes of Porphyrinoids

J. SETSUNE, M. TODA and T. YOSHIDA, *Chem. Commun.*, 2008, (12), 1425–1427

Multinuclear Rh complexes of the large porphyrinoids expanded rosarin and octaphyrin having the 1,4-phenylene spacers where the Rh(CO)₂ group passes through the macrocycle were synthesised. The Rh₃ complex of the expanded rosarin exists as the C_{3v}-isomer in CH₂Cl₂ as well as in the crystal state. Relatively slow metal transposition passing through macrocycle was observed in toluene solution to cause interchange between the C_{3v}-isomer and the C_s-isomer. Four metals are fixed in the Rh₄ complex of the expanded octaphyrin.

ELECTRICAL AND ELECTRONICS

Nanomechanical and Nanotribological Characterization of Noble Metal-Coated AFM Tips for Probe-Based Ferroelectric Data Recording

M. PALACIO and B. BHUSHAN, *Nanotechnology*, 2008, 19, (10), 105705 (9 pages)

Nanoindentation experiments were carried out to evaluate the mechanical properties of Pt, Pt-Ni, Au-Ni and Pt-Ir deposited on AFM probes. The Pt-Ir coating exhibited the highest hardness, highest elastic modulus and lowest creep resistance. Nanoscratch studies revealed that the noble metal coatings are removed primarily by plastic deformation.

ELECTROCHEMISTRY

Degradation Characteristics of IrO₂-type DSA[®] in Methanol Aqueous Solutions

J.-M. HU, X.-J. SUN, Y.-Y. HOU, J.-Q. ZHANG and C.-N. CAO, *Electrochim. Acta*, 2008, 53, (7), 3127–3138

A comparative study was done on the long-term stability and deactivation characteristics of Ti/IrO₂-type dimensionally stable anodes (1) in acidic solutions in the absence and the presence of MeOH, respectively. The service life increased and then decreased as the calcination temperature of the as-prepared (1) was increased. The lifetime was shortened by the addition of MeOH into the testing solution.

PHOTOCONVERSION

The Influence of Platinum on UV and 'Visible' Photocatalysis by Rutile and Degussa P25

T. A. EGERTON and J. A. MATTINSON, *J. Photochem. Photobiol. A: Chem.*, 2008, 194, (2–3), 283–289

The influence of Pt on the UV photocatalytic degradation of the dichloroacetate anion (DCA) by rutile and the P25 form of TiO₂ was investigated. The Pt was deposited photochemically. Although the catalytic activity of rutile was much less than that of the P25, the effect of Pt addition was so much greater on rutile than on P25 that the activities of the Pt-treated titanias were similar. Visible light irradiation of Pt/rutile oxidised the DCA.

Single Dopant White Electrophosphorescent Light Emitting Diodes Using Heteroleptic Tris-Cyclometalated Iridium(III) Complexes

J. H. SEO, I. J. KIM, Y. K. KIM and Y. S. KIM, *Thin Solid Films*, 2008, 516, (11), 3614–3617

A single dopant single emissive layer white organic electroluminescent (EL) device (1) was based on Ir(dfppy)₂(pq) (dfppy = 2-(2,4-difluorophenyl)pyridine, pq = 2-phenylquinoline) as the guest and 1,4-phenylenebis(triphenylsilane) as the host. The maximum luminous and power efficiencies of (1) were 11.00 cd A⁻¹ (*J* = 0.05 mA cm⁻²) and 5.60 lm W⁻¹ (*J* = 0.001 mA cm⁻²), respectively. The CIE coordinates of (1) are (0.443, 0.473) and the EL spectrum of (1) shows emission bands at 473 and 544 nm, at the applied voltage of 12 V.

Exploitation of the Dual-emissive Properties of Cyclometalated Iridium(III)-Polypyridine Complexes in the Development of Luminescent Biological Probes

K. K.-W. LO, K. Y. ZHANG, S.-K. LEUNG and M.-C. TANG, *Angew. Chem. Int. Ed.*, 2008, 47, (12), 2213–2216

In polar and nonpolar media the title complexes show green and orange-yellow emission, respectively. The incorporation of biological substrates into this system results in luminescent probes that exhibit pronounced changes in their emission profiles upon binding to their specific receptors. Novel luminescent biological probes for avidin, oestrogen receptor α and human serum albumin have been developed.

SURFACE COATINGS

The Electrodeposition and Electrocatalytic Properties of Copper–Palladium Alloys

C. MILHANO and D. FLETCHER, *J. Electroanal. Chem.*, 2008, 614, (1–2), 24–30

The codeposition of Cu and Pd from CuSO₄ and PdSO₄ in HClO₄ was investigated using microdisc voltammetry. Good quality coatings of CuPd were deposited. The composition of the coatings was controlled either through the deposition potential or the Cu(II):Pd(II) ratio in solution.