

ABSTRACTS

CATALYSIS – APPLIED AND PHYSICAL ASPECTS

Comparative Study of Aromatization Selectivity During *n*-Heptane Reforming on Sintered Pt/Al₂O₃ and Pt-Re/Al₂O₃ Catalysts

A. A. SUSU, *J. Chem. Technol. Biotechnol.*, 2008, 83, (6), 928–942

The main products of *n*-heptane reforming on fresh Pt were CH₄, toluene and benzene, while on fresh Pt-Re, only CH₄ was obtained. For Pt/Al₂O₃, the products ranged from only toluene at a sintering temperature (ST) of 500°C to CH₄ at a ST of 650°C, with no reaction at 800°C. On Pt-Re/Al₂O₃, CH₄ was the sole product at a ST of 500°C while only toluene was produced at a ST of 800°C. Pt-Re/Al₂O₃ exhibited superior selectivity.

Carbon-Carbon Cross-Coupling Reactions under Continuous Flow Conditions Using Poly(vinylpyridine) Doped with Palladium

K. MENNECKE, W. SOLODENKO and A. KIRSCHNING, *Synthesis*, 2008, (10), 1589–1599

The coordinative immobilisation of an oxime-based palladacycle to PVP/glass composites shaped as Raschig rings or placed within a PASSflow™ microreactor affords devices that can be used for Pd-catalysed C–C cross-coupling in the flow-through mode. Reusability of the immobilised precatalyst as well as reactions in the microwave field were investigated.

CATALYSIS – INDUSTRIAL PROCESS

Development of a Mild and Robust Method for Large-Scale Palladium-Catalysed Cyanation of Aryl Bromides: Importance of the Order of Addition

P. RYBERG, *Org. Process Res. Dev.*, 2008, 12, (3), 540–543

The title reaction is sensitive to cyanide poisoning of the catalyst. For Pd(dba)₂ + P(^tBu)₃, the order of adding the reagents affected the performance of the reaction. Addition of the cyanide source (Zn(CN)₂) to a preheated mixture of the aryl bromide, catalyst and Zn dust was found to be critical. This reaction could be run to full conversion within 3 h at 50°C on a 6.7 kg scale. New efficient catalysts were identified.

CATALYSIS – REACTIONS

Enhancing H₂ and CO Production from Glycerol Using Bimetallic Surfaces

O. SKOPLYAK, M. A. BARTEAU and J. G. CHEN, *ChemSusChem*, 2008, 1, (6), 524–526

TPD experiments revealed an increased production of H₂ from glycerol on the Ni surface monolayer on Pt(111) (designated Ni-Pt-Pt(111)) as compared to that on Pt(111), Ni(111) and Pt-Ni-Pt(111). Glycerol reforming activity trends were similar to previous results for ethylene glycol and EtOH. Smaller oxygenates can therefore be used as good models for reforming of larger, biomass-derived oxygenates.

Efficient and Recyclable Catalyst of Palladium Nanoparticles Stabilized by Polymer Micelles Soluble in Water for Suzuki-Miyaura Reaction, Ostwald Ripening Process with Palladium Nanoparticles

I. P. BELETSKAYA, A. N. KASHIN, I. A. KHOTINA and A. R. KHOKHLOV, *Synlett*, 2008, (10), 1547–1552

The Suzuki-Miyaura cross-coupling of ArX (X = I, Br) with Ar'B(OH)₂, catalysed by a Pd-containing H₂O-soluble micelle formed by PS-PEO and *N*-cetylpyridinium chloride, was investigated in H₂O and MeOH. The reaction was performed at ≤ 50°C. The catalyst can be recycled (5 runs) by ultrafiltration.

Direct Coupling of Arenes and Iodoarenes Catalyzed by a Rhodium Complex with a Strongly π -Accepting Phosphite Ligand

S. YANAGISAWA, T. SUDO, R. NOYORI and K. ITAMI, *Tetrahedron*, 2008, 64, (26), 6073–6081

A solution of [RhCl(CO)₂]₂ and P[OCH(CF₃)₂]₃ in dry toluene was stirred at 50°C for 2 h under Ar to synthesise RhCl(CO){P[OCH(CF₃)₂]₃}₂ (1). Under the catalytic influence of (1) and Ag₂CO₃, the direct C–H arylation of heteroarenes and arenes with iodoarenes was achieved. The product biaryls were obtained in good to excellent yields with high regioselectivity. This method can be used for thiophenes, furans, pyrroles, indoles and alkoxybenzenes.

Vinyl and Ring-Opening Metathesis Polymerization of Norbornene with Novel Half-Sandwich Iridium(III) Complexes Bearing Hydroxyindanimine Ligands

X. MENG, G.-R. TANG and G.-X. JIN, *Chem. Commun.*, 2008, (27), 3178–3180

Half-sandwich Ir(III) complexes bearing hydroxyindanimine ligands were synthesised. The complexes were used as catalysts for the ROMP and vinyl-type polymerisation of norbornene in the presence of methylaluminoxane (MAO). Pure ROMP polymer and vinyl-type polymer were obtained depending on the amount of MAO employed (0–30 equiv. for ROMP and > 30 equiv. for vinyl-type polymerisation).

EMISSIONS CONTROL

Impact of Redox Conditions on Thermal

Deactivation of NO_x traps for Diesel

K. M. ADAMS and G. W. GRAHAM, *Appl. Catal. B: Environ.*, 2008, 80, (3–4), 343–352

Lean and rich agings were investigated for a model NO_x trap, Pt-Ba/Al₂O₃. These were carried out at 950°C for 3 h, in air and in 1% H₂/N₂, respectively. Pretreatments were examined for a commercially feasible NO_x trap and two model NO_x traps, Pt-Ba/Al₂O₃ and Pt-Ba-Ce/Al₂O₃, at 600°C for 10 min, using feed gas that simulated diesel exhaust under various conditions.

Enhanced Degradation of Tetrachloroethylene by Green Rusts with Platinum

J. CHOI and W. LEE, *Environ. Sci. Technol.*, 2008, 42, (9), 3356–3362

The reductive dechlorination of tetrachloroethylene (PCE) by green rusts (GRs) (layered Fe(II)–Fe(III) hydroxide solids with anions such as Cl^- , SO_4^{2-} , CO_3^{2-} , F^-) in the presence of Pt was carried out using a batch reactor system. The rate of PCE reduction was greatly enhanced with the addition of Pt(IV) (95% of PCE was removed in 30 h). PCE was mostly transformed to acetylene. The estimated kinetic rate constants of GR-Cl(Pt) increased significantly with an incremental addition of Pt from 0.5 to 2 mM.

FUEL CELLS

Application of Atomic Layer Deposition of Platinum to Solid Oxide Fuel Cells

X. JIANG, H. HUANG, F. B. PRINZ and S. F. BENT, *Chem. Mater.*, 2008, 20, (12), 3897–3905

Atomic layer deposition (ALD) was used to deposit Pt thin films as an electrode/catalyst layer for SOFCs. The measured fuel cell performance showed that comparable peak power densities were achieved for ALD-deposited Pt anodes with only one-fifth of the Pt loading relative to dc-sputtered Pt anodes. A micropatterned Pt structure was fabricated *via* area-selective ALD and used as a current collector grid/patterned catalyst for the fuel cells.

Platinum Black Polymer Electrolyte Membrane Based Electrodes Revisited

L. KRISHNAN, S. E. MORRIS and G. A. EISMAN, *J. Electrochem. Soc.*, 2008, 155, (9), B869–B876

Pt black-coated diffusion media of varying anode and cathode catalyst loadings with H_2 /air demonstrated successful performance and stability for anode catalyst loadings down to 0.25 mg cm^{-2} while operating on pure H_2 and with a cathode loading of 0.62 mg cm^{-2} , without significant voltage losses. The voltage losses from reducing the Pt black cathode loadings (from 2.6 to 0.62 mg cm^{-2}) are consistent with kinetic losses associated with the O_2 reduction reaction and lower electrocatalyst utilisation. Optimisation of the three-phase interface – electrode, electrolyte and reactant gas – was shown to be dependent on the efficacy of the membrane–catalyst layer interface.

The Improved Methanol Tolerance Using Pt/C in Cathode of Direct Methanol Fuel Cell

Y.-H. CHO, H.-S. PARK, Y.-H. CHO, I.-S. PARK and Y.-E. SUNG, *Electrochim. Acta*, 2008, 53, (20), 5909–5912

MEAs were prepared using PtRu black and 60 wt.% Pt/C as their anode and cathode catalysts, respectively. The cathode catalyst layers were fabricated using 0.5, 1.0, 2.0 and 3.0 mg cm^{-2} of Pt. The performance of the single cell that used Pt/C as the cathode catalyst was higher than a single cell that used Pt black; this result was pronounced when highly concentrated MeOH ($> 2.0 \text{ M}$) was used as the fuel.

Graphite Nanofibers as Catalyst Support for Proton Exchange Membrane Fuel Cells

H. XU, L. LU and S. ZHU, *Chin. J. Catal.*, 2008, 29, (6), 542–546

Graphite nanofibres (GNFs) were prepared from used C paper by a ball-milling method. 20% Pt was loaded on the GNFs and Vulcan XC-72 to fabricate Pt/GNFs and Pt/XC-72, respectively. CV showed that Pt/GNFs had the same electrochemical surface area (ESA) as Pt/XC-72. The electrochemical stability was measured for XC-72, GNFs, Pt/XC-72 and Pt/GNFs electrodes by the constant potential oxidation. The peak current increased by 2% for GNFs and 60% for XC-72. The corrosion current for Pt/XC-72 was 1.4 times of that for Pt/GNFs. 84.7% ESA was lost for Pt/XC-72 after oxidation for 60 h, while only 37.2% ESA was lost for Pt/GNFs.

METALLURGY AND MATERIALS

Purification of Iridium by Electron Beam Melting

E. K. OHRINER, *J. Alloys Compd.*, 2008, 461, (1–2), 633–640

The purification of Ir metal by electron beam melting has been characterised for 48 impurity elements. The average levels of individual elemental impurities in the starting Ir powder varied from $37 \mu\text{g g}^{-1}$ to $0.02 \mu\text{g g}^{-1}$. Li, Na, Mg, P, S, Cl, K, Ca, Mn, Co, Ni, Cu, Zn, As, Pd, Ag, Cd, Sn, Sb, Te, Ba, Ce, Tl, Pb and Bi were not detectable following the purification. No significant change in the concentration of Ti, V, Zr, Nb, Mo and Re was found. B, C, Al, Si, Cr, Fe, Ru, Rh and Pt were partially removed by vapourisation.

Effects of Alloying Elements on Dendritic Segregation in Iridium Alloys

Y. LIU, C. T. LIU, L. HEATHERLY and E. P. GEORGE, *J. Alloys Compd.*, 2008, 459, (1–2), 130–134

The effects of alloying elements on dendritic segregation in 'Ir-Nb' (Ir-10Nb-0.5Zr-0.3W-0.3C-0.006Th, at.%) and 'Ir-Zr' (Ir-4.5Zr-0.3W-0.3C-0.006Th, at.%) alloys were investigated by Auger electron spectroscopy. The Nb addition induces significant segregation of C and Th to dendritic interfaces. The Zr addition leads to the formation of an Ir;Zr intermetallic phase, which results in less dendritic segregation of C and Th. This dendritic segregation may cause the severe cracking observed in the 'Ir-Nb' alloy after casting and heat treatment.

Synthesis of Ruthenium Particles by Photoreduction in Polymer Solutions

M. HARADA and S. TAKAHASHI, *J. Colloid Interface Sci.*, 2008, 325, (1), 1–6

Colloidal dispersions of poly(*N*-vinyl-2-pyrrolidone)-protected Ru particles were conveniently and efficiently synthesised by the photoreduction of Ru(III) ionic solutions (using $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$) in the presence of a photoactivator. Metallic Ru particles (1.3 nm average diameter) were obtained in the presence of benzophenone, although mixtures of partly oxidised Ru particles and metallic Ru particles were produced in the presence of benzoic acid.

APPARATUS AND TECHNIQUE

Determination of Alcohols Using a Ni–Pt Alloy Amperometric Sensor

J.-J. HUANG, W.-S. HWANG, Y.-C. WENG and T.-C. CHOU, *Thin Solid Films*, 2008, 516, (16), 5210–5216

Ni–Pt films were electrodeposited on Au/Al₂O₃. Electrodes with Ni:Pt atomic proportions of 100:0, 25:75, 70:30, 82:18 and 0:100 all have a linear relationship between response current and EtOH concentration for 50–300 ppm EtOH in alkaline solutions. With increasing Pt content, the response time was reduced and the sensitivity was decreased. The sensor with 70 at.% Pt was most stable (9 weeks).

A Multi-Walled Carbon Nanotube/Palladium Nanocomposite Prepared by a Facile Method for the Detection of Methane at Room Temperature

Y. LI, H. WANG, Y. CHEN and M. YANG, *Sens. Actuators B: Chem.*, 2008, 132, (1), 155–158

A composite (1) of Pd and C MWNTs was prepared by reducing their aqueous mixtures with NaBH₄. TEM and AFM were used to investigate the morphology of (1). The electrical responses of (1) to CH₄ were measured at room temperature. (1) exhibited a response magnitude of ~ 4.5% towards 2% CH₄.

BIOMEDICAL AND DENTAL

Influence of the Spacer Length on the *in Vitro* Anticancer Activity of Dinuclear Ruthenium–Arene Compounds

M.-G. MENDOZA-FERRI, C. G. HARTINGER, R. E. EICHINGER, N. STOLYAROVA, K. SEVERIN, M. A. JAKUPEC, A. A. NAZAROV and B. K. KEPPLER, *Organometallics*, 2008, 27, (11), 2405–2407

The title complexes exhibited promising cytotoxic effects in human cancer cells, which could be increased to an IC₅₀ of 0.29 μM by increasing the spacer length between the metal centres. Cytotoxicity could be correlated with lipophilicity and H₂O solubility. 1,12-Bis{chlorido[3-(oxo-κO)-2-methyl-4-pyridinonato-κO4]}(η⁶-*p*-isopropyltoluene)ruthenium} dodecane is more active than chlorido[3-(oxo-κO)-2-methyl-4-pyridonato-κO4]}(η⁶-*p*-isopropyltoluene)ruthenium.

Novel Ru(II) Oximate Complexes with Silent Oxygen Atom: Synthesis, Chemistry and Biological Activities

N. CHITRAPRIYA, V. MAHALINGAM, L. C. CHANNELS, M. ZELLER, F. R. FRONCZEK and K. NATARAJAN, *Inorg. Chim. Acta*, 2008, 361, (9–10), 2841–2850

[Ru(CO)(EPh₃)₂(bhmh)] (E = P or As; H₂bhmh = benzoic acid (2-hydroxyimino-1-methyl-propylidene)-hydrazide), [Ru(CO)(EPh₃)₂(ihmh)] (H₂ihmh = isonicotinic acid (2-hydroxyimino-1-methyl-propylidene)-hydrazide) and [Ru(CO)(EPh₃)₂(hhmh)] (H₂hhmh = 2-hydroxy-benzoic acid (2-hydroxyimino-1-methyl-propylidene)-hydrazide) were prepared. The hydrazone ligand coordinates through the N atoms of the imine and oxime and the O atom of the amide. The N–OH moiety of the oxime is deprotonated. Antibacterial activity and DNA-binding ability of the complexes were investigated.

CHEMISTRY

RuO₂–TiO₂ Mixed Oxides Prepared From the Hydrolysis of the Metal Alkoxides

J. R. OSMAN, J. A. CRAYSTON, A. PRATT and D. T. RICHENS, *Mater. Chem. Phys.*, 2008, 110, (2–3), 256–262

Ru alkoxide/Ti tetraethoxide mixtures were hydrolysed to give gels and powders containing 30–40 mol% Ru. Basic or neutral conditions gave powders consisting of crystalline RuO₂ nanoparticles (2–10 nm diameter) embedded in a matrix of crystalline (anatase) and amorphous TiO₂. Acid hydrolysis conditions led to gels containing smaller, amorphous RuO₂ nanoparticles (1–3 nm). Acid or neutral hydrolysis of Ru ethoxide gave samples with lower surface Ru:Ti ratios compared to the bulk, which also contained more low-valent Ru.

ELECTRICAL AND ELECTRONICS

Synthesis of Ru/Multiwalled Carbon Nanotubes by Microemulsion for Electrochemical Supercapacitor

S. YAN, P. QU, H. WANG, T. TIAN and Z. XIAO, *Mater. Res. Bull.*, 2008, 43, (10), 2818–2824

Ru nanoparticles were prepared by H₂O-in-oil reverse microemulsion, and then anchored on C MWNTs. EDX spectra confirmed the presence of Ru oxide in the as-prepared composites after electrochemical oxidation. CV demonstrated that the specific capacitance of deposited Ru oxide electrode was significantly greater than that of a C MWNTs electrode.

PHOTOCONVERSION

Phosphorescent Iridium(III) Complexes with Nonconjugated Cyclometalated Ligands

Y.-H. SONG, Y.-C. CHIU, Y. CHI, Y.-M. CHENG, C.-H. LAI, P.-T. CHOU, K.-T. WONG, M.-H. TSAI and C.-C. WU, *Chem. Eur. J.*, 2008, 14, (18), 5423–5434

Ir(III) complexes (1–4) with nonconjugated *N*-benzylpyrazole ligands exhibit blue phosphorescence with yields of 5–45 % in degassed CH₂Cl₂. (1) showed emission that was nearly true blue at 460 nm with a lack of vibronic progression. (1) was used as the host for the green-emitting Ir(ppy)₃ dopant in an OLED.

REFINING AND RECOVERY

Synthesis of Highly Porous Chitosan Microspheres Anchored with 1,2-Ethylenedisulfide Moiety for the Recovery of Precious Metal Ions

Y. KANAI, T. OSHIMA and Y. BABA, *Ind. Eng. Chem. Res.*, 2008, 47, (9), 3114–3120

Highly porous chitosan microspheres (EDSC) with large pores anchoring 1,2-ethylenedisulfide as a ligand were synthesised for perfusion chromatography by means of an oil-in-H₂O-in-oil emulsion method. EDSC was found to be a selective adsorbent for Pd(II), Au(III) and Pt(IV) over base metals in HCl. The adsorbed Pd(II) was completely desorbed using aqueous thiourea solution.