

ABSTRACTS

CATALYSIS – REACTIONS

Development of an Amphiphilic Resin-Dispersion of Nanopalladium and Nanoplatinum Catalysts: Design, Preparation, and Their Use in Green Organic Transformations

Y. UOZUMI and Y. M. A. YAMADA, *Chem. Rec.*, 2009, 9, (1), 51–65

An amphiphilic polystyrene-poly(ethylene glycol) resin-dispersion of Pd nanoparticles exhibited high catalytic performance in the hydrodechlorination of chloroarenes under aqueous conditions. Amphiphilic resin-supported Pd and Pt nanoparticle catalysts were active for the aerobic oxidation of alcohols in H₂O under an atmospheric pressure of O_{2(g)}.

Preparation of Nano-Pd/SiO₂ by One-Step Flame Spray Pyrolysis and Its Hydrogenation Activities: Comparison to the Conventional Impregnation Method

O. MEKASUWANDUMRONG, S. SOMBOONTHANAKIJ, P. PRASERTHDAM and J. PANPRANOT, *Ind. Eng. Chem. Res.*, 2009, 48, (6), 2819–2825

Nano-Pd/SiO₂ catalysts synthesised in one-step flame spray pyrolysis (FSP) were compared to those on flame-made SiO₂ supports by conventional impregnation. Metallic Pd particles < 3 nm in size were obtained directly by one-step FSP, while impregnation gave PdO with crystallite sizes 5–12 nm. TOF values for 1-heptyne hydrogenation on the one-step FSP catalysts decreased from 66.2 s⁻¹ to 4.3 s⁻¹ as Pd loading increased from 0.5 wt.% to 10 wt.%.

Steam Reforming of Methane, Ethane, Propane, Butane, and Natural Gas over a Rhodium-Based Catalyst

B. T. SCHÄDEL, M. DUISBERG and O. DEUTSCHMANN, *Catal. Today*, 2009, 142, (1–2), 42–51

Steam reforming (SR) was investigated over a Rh-based cordierite monolithic honeycomb catalyst. The product distribution was analysed as a function of temperature (250–900°C) and steam-to-carbon ratio (2.2–4) for two honeycomb channel densities (600 and 900 cpsi) and an uncoated monolith. Ethane, propane, and butane are converted at much lower temperature than methane, also in the natural gas mixtures.

EMISSIONS CONTROL

Reduction of NO_x by H₂ on Pt/WO₃/ZrO₂ Catalysts in Oxygen-Rich Exhaust

F. J. P. SCHOTT, P. BALLE, J. ADLER and S. KURETI, *Appl. Catal. B: Environ.*, 2009, 87, (1–2), 18–29

Pt/WO₃/ZrO₂ (1) with a Pt loading of 0.3 wt.% and a W content of 11 wt.% had high deNO_x activity below 200°C and high overall N₂ selectivity. Additionally, (1) exhibited outstanding hydrothermal stability and resistance against SO_x.

Synthesis and Characterization of Rh and RhO_x Particles Supported on Zeolites with High Activity of Lean NO_x-CO-H₂ Reaction

T. NAKATSUJI, T. YAMAGUCHI, J. LI, N. SATO and Y. MATSUZONO, *Catal. Commun.*, 2009, 10, (6), 763–767

Rh and RhO_x nanoparticles supported on zeolites were synthesised in a hydrothermal process using a gel mixture of zeolite and Rh precursors. The nanoparticles loaded onto Na-β zeolite and Na-ZSM-5 as dispersed particles and agglomerated particles, respectively. The nanoparticles supported on Na-ZSM-5 are more efficient in catalysing NO_x reduction in lean conditions using H₂ and CO.

FUEL CELLS

Quantitative Characterization of Catalyst Layer Degradation in PEM Fuel Cells by X-Ray Photoelectron Spectroscopy

F.-Y. ZHANG, S. G. ADVANI, A. K. PRASAD, M. E. BOGGS, S. P. SULLIVAN and T. P. BEEBE Jr., *Electrochim. Acta*, 2009, 54, (16), 4025–4030

The elemental concentrations and chemical states of C, F, Pt, O and S on a PEM fuel cell catalyst layer were determined by XPS. XPS signals characteristic of the ionomer decrease after ~ 300 h of fuel cell operation. Ionomer degradation was characterised by a decrease of CF₃ and CF₂ species and an increase in oxidised forms of C. The surface concentrations of F and Pt decreased from 50.1% to 38.9%, and from 0.4% to 0.3%, respectively. The oxidized states of Pt and C were substantially higher for the used samples.

Kinetics of Oxygen Reduction Reaction on

Co^{rich} core-Pt^{rich} shell/C Electrocatalysts

M. H. LEE and J. S. DO, *J. Power Sources*, 2009, 188, (2), 353–358

Prepared nanosized Pt/C (1) and Co^{rich} core-Pt^{rich} shell/C (2) were shown to have the same f.c.c. crystal structure by XRD, and their mean particle sizes (TEM) were 3.58 and 4.12 nm, respectively. The mass activity and specific activity of the ORR on (2) were 10.22 A g⁻¹ and 2.73 × 10⁻⁵ A cm⁻², which were 1.5 and 1.8 times those of the ORR on (1). The kinetics of the ORR on (1) and (2) in 0.5 M HClO₄ were examined using film-type electrocatalysts on a RDE.

Deactivation/Reactivation of a Pd/C Catalyst in a Direct Formic Acid Fuel Cell (DFAFC): Use of Array Membrane Electrode Assemblies

X. YU and P. G. PICKUP, *J. Power Sources*, 2009, 187, (2), 493–499

A multi-anode, liquid-fed fuel cell was developed for the study of DFAFC anode catalysts. Deactivation of Pd/C is caused by the electrooxidation of the formic acid, and does not occur significantly at open circuit. Deactivated anodes were shown to only be electrochemically reactivated by reversing the cell voltage. Reactivation is slow (> 1 min) if the voltage is less negative than -0.2 V.

METALLURGY AND MATERIALS

Halogen-Induced Corrosion of Platinum

E. DONÁ, M. CORDIN, C. DEISL, E. BERTEL, C. FRANCHINI, R. ZUCCA and J. REDINGER, *J. Am. Chem. Soc.*, 2009, 131, (8), 2827–2829

The interaction of Cl with Pt(110) was studied in an ultrahigh vacuum environment. Up to half a monolayer of Cl formed an adsorbate structure. Compression to higher local coverages led to erosion of Pt atoms from the top layer and formation of PtCl₄ pentamers. The Pt defects healed after annealing and a long-range-ordered PtCl₄/Cl/Pt(110) adlayer was formed. Coadsorption of the Cl layer with CO caused formation of PtCl₄ but no volatile compounds.

The Role of Destabilization of Palladium Hydride in the Hydrogen Uptake of Pd-Containing Activated Carbons

V. V. BHAT, C. I. CONTESCU and N. C. GALLEG0, *Nanotechnology*, 2009, 20, (20), 204011 (10 pages)

A sample containing Pd embedded in activated C fibre (2 wt.% Pd) was compared with commercial Pd nanoparticles deposited on microporous activated C (3 wt.% Pd) and with nanocrystalline Pd. The phase transformations were analysed over 0.003–10 bar H₂ partial pressures and at several temperatures using *in situ* XRD. Volumetric H₂ uptake measurements verified these results. Higher degrees of Pd–C contacts for Pd particles embedded in the microporous C matrix induce efficient ‘pumping’ of H out of β-PdH_x. Thermal cleaning of C surface groups prior to H₂ exposure further enhances the H pumping power of the microporous C.

Rietveld Analysis of Neutron Powder Diffraction of Mg₆Pd Alloy at Various Hydriding Stages

J. HUOT, A. YONKEU and J. DUFOUR, *J. Alloys Compd.*, 2009, 475, (1–2), 168–172

Mg₆Pd alloy was obtained by ball milling from rolled Mg and small pieces of Pd foil. The evolution of the crystal structure of Mg₆Pd was studied by simultaneous Rietveld refinement of the neutron and X-ray powder diffraction data. Samples with different D contents were measured, corresponding to reaction end-products of the proposed hydrogenation step. After full hydrogenation, Mg₆Pd transforms to MgPd and MgD₂. Increases in lattice parameters of MgPd alloy agree well with measured H capacities.

New Hard and Superhard Materials: RhB_{1.1} and IrB_{1.35}

J. V. RAU and A. LATINI, *Chem. Mater.*, 2009, 21, (8), 1407–1409

Phase-pure RhB_{1.1} and IrB_{1.35} bulk materials were prepared using an electron beam apparatus. Powder XRD patterns for both borides were obtained; the Rietveld analysis results are presented. The Vickers microhardness data revealed the superhard nature of IrB_{1.35}: under 0.49 N of applied load, it exhibits a maximum hardness of 49.8 ± 6.0 GPa. RhB_{1.1} bulk was found to be hard: under 0.49 N of applied load, it exhibits a hardness of 22.6 ± 1.5 GPa.

CHEMISTRY

An Old Reaction in New Media: Kinetic Study of a Platinum(II) Substitution Reaction in Ionic Liquids

I. CORREIA and T. WELTON, *Dalton Trans.*, 2009, (21), 4115–4121

A kinetic study was carried out on the substitution reaction of [Pt(dpma)Cl]⁺ with thioacetate in room temperature ionic liquids and molecular solvents. The reaction follows an associative mechanism with a two-term rate law and is the same in all the solvents studied. The reaction rate followed the order: H₂O > ionic liquids and DMSO > methanol. No ‘ionic liquid effect’ was found.

Studies on the Complexation between Generation-4.5 Methyl Ester-Terminated Poly(amidoamine) Dendrimer and Pd²⁺ Ions in Methanol

W. LU, G. LI, Y. LUO and Y. JIN, *J. Appl. Polym. Sci.*, 2009, 112, (5), 2854–2858

The interactions between Pd²⁺ ions and G4.5-COOCH₃ PAMAM dendrimers were investigated by UV-vis and FTIR. The addition of K₂PdCl₄ results in covalent attachment of the PdCl₃⁻ alcoholysis product of this complex to tertiary amines within the dendrimers under the appropriate conditions. XPS data indicated a 1:3 Pd:Cl ratio. The maximum loading of Pd²⁺ ions within the G4.5-COOCH₃ dendrimers was 80. The best pH value for complexation was 8.3.

Synthesis and Characterization of Water-Soluble Palladium(II)-Functionalized Diphosphine Complexes

M. SUNJUK, M. AL-NOAIMI, G. ABU SHEIKHA, E. LINDNER, B. EL-ESWED and K. SWEIDAN, *Polyhedron*, 2009, 28, (8), 1393–1398

H₂O-soluble *cis*-[Pd(L)(OAc)₂] (1) (L = CH₂(CH₂PR₂)₂ and R = (CH₂)₆OH; (CH₂)_nP(O)(OEt)₂, n = 2–6 or 8; or (CH₂)₃NH₂) were obtained by reacting Pd(OAc)₂ with L in a 1:1 mixture of CH₂Cl₂:CH₃CN. L were prepared photochemically by hydrophosphination of the corresponding 1-alkenes with H₂P(CH₂)₃PH₂.

PHOTOCONVERSION

A Versatile Color Tuning Strategy for Iridium(III) and Platinum(II) Electrophosphors by Shifting the Charge-Transfer States with an Electron-Deficient Core

G.-J. ZHOU, Q. WANG, W.-Y. WONG, D. MA, L. WANG and Z. LIN, *J. Mater. Chem.*, 2009, 19, (13), 1872–1883

Red cyclometallated Ir(III) and Pt(II) electrophosphors with enhanced electron-injection/electron-transporting features were prepared by using an electron-trapping fluoren-9-one chromophore. There is a switch of the MLCT character of the transition from the pyridyl groups in the traditional Ir(III) and Pt(II) ppy-type complexes to the electron-deficient ring core. The electron-withdrawing character of the fused ring results in more stable MLCT states, inducing a substantial red-shift of the triplet emission energy from yellow to red for the Ir(III) complex and even green to red for the Pt(II) complex.