

ABSTRACTS

CATALYSIS – APPLIED AND PHYSICAL ASPECTS

Quantitative Analysis of Transient Surface Reactions on Planar Catalyst with Time-Resolved Time-of-Flight Mass Spectrometry

K. OKUMURA, Y. SAKAMOTO, T. KAYAMA, Y. KIZAKI, H. SHINJOH and T. MOTOHIRO, *Rev. Sci. Instrum.*, 2007, 78, (10), 104102 (9 pages)

The title analysis employed pulsed-gas valves for the injection of reactant molecules. The products of NO + H₂ reaction on a planar catalyst, Pt–Al₂O₃/Si substrates inserted into a micro tube reactor with SiC balls, were analysed. The procedure enabled analysis of the transient consecutive secondary catalytic reactions as well as primary reactions based on the formation rate of product molecules per millisecond.

Platinum Nanoparticles Supported on Ionic Liquid-Modified Magnetic Nanoparticles: Selective Hydrogenation Catalysts

R. ABU-REZIQ, D. WANG, M. POST and H. ALPER, *Adv. Synth. Catal.*, 2007, 349, (13), 2145–2150

Pt nanoparticles were supported on magnetic nanoparticles modified with ionic liquid groups, by adsorbing K₂PtCl₄ on the surface of magnetite nanoparticles *via* ion exchange with the linked ionic liquid groups, and then reducing using hydrazine. The obtained catalyst (1) was used for the selective hydrogenation of alkynes and α,β -unsaturated aldehydes. (1) can be separated by an external magnetic field.

Characterization of Metal Segregation in Pt–Re/Al₂O₃ Reforming Catalysts

YU. V. GURYEV, I. I. IVANOVA, V. V. LUNIN, W. GRÜNERT and M. W. E. VAN DEN BERG, *Appl. Catal. A: Gen.*, 2007, 329, 16–21

Mono- and bimetallic Pt–Re catalysts (1) with 0.3 wt.% of each metal were investigated. The combination of H₂ and O₂ chemisorption techniques was demonstrated to be a sensitive tool to monitor Pt–Re interaction. The presence of H₂O on (1) during high-temperature treatments was a major factor affecting Pt and Re aggregation and segregation.

Role of Gas-Phase Chemistry in the Rich Combustion of H₂ and CO over a Rh/Al₂O₃ Catalyst in Annular Reactor

M. MAESTRI, A. BERETTA, T. FARAVELLI, G. GROPPI and E. TRONCONI, *Chem. Eng. Sci.*, 2007, 62, (18–20), 4992–4997

A 2D isothermal model was used to analyse H₂- and CO-rich combustions over Rh/Al₂O₃. As found experimentally, homogeneous ignition of H₂/O₂ was predicted to occur above 650°C, whereas this did not occur for CO/O₂ (only heterogeneously consumed). For both reaction systems, there were intermediate temperature windows where the observed conversions exceeded the diffusion limit.

CATALYSIS – INDUSTRIAL PROCESS

Catalytic Conversion of Waste Plastics: Focus on Waste PVC

M. A. KEANE, *J. Chem. Technol. Biotechnol.*, 2007, 82, (9), 787–795

The efficacy of Pd/Al₂O₃ to promote the catalytic dechlorination of PVC was demonstrated. A significant decrease (by a factor of up to 560) in the liquid fraction Cl content is seen; in addition to differences (relative to thermal degradation) in the gas phase product, i.e. higher C₁–C₄ content with preferential alkane formation.

CATALYSIS – REACTIONS

Palladium Supported on Poly(*N*-vinylimidazole) or Poly(*N*-vinylimidazole-*co*-*N*-vinylcaprolactam) as a New Recyclable Catalyst for the Mizoroki-Heck Reaction

I. P. BELETSKAYA, A. R. KHOKHLOV, E. A. TARASENKO and V. S. TYURIN, *J. Organomet. Chem.*, 2007, 692, (20), 4402–4406

The high efficiency and stability of the title catalytic system (1) was demonstrated in the Mizoroki-Heck reaction with active (aryl iodides and *n*-butyl acrylate) and less active (aryl bromides and styrene) substrates. The reaction proceeded faster using the copolymer rather than the homopolymer. (1) could be recycled.

Supercritical Carbon Dioxide and Poly(ethylene glycol): An Environmentally Benign Biphasic Solvent System for Aerobic Oxidation of Styrene

J.-Q. WANG, F. CAI, E. WANG and L.-N. HE, *Green Chem.*, 2007, 9, (8), 882–887

Aerobic oxidation of styrene catalysed by PdCl₂/CuCl can be carried out in a scCO₂ and PEG biphasic system. A high yield of acetophenone was obtained. The PdCl₂-mediated oxidation of styrene preferentially yielded benzaldehyde using the biphasic scCO₂/PEG system. Product separation and catalyst recycling are possible.

EMISSIONS CONTROL

Estimating the Temperatures of the Precious Metal Sites on a Lean NO_x Trap during Oxidation Reactions

J. R. THEIS and E. GULARI, *Appl. Catal. B: Environ.*, 2007, 75, (1–2), 39–51

The temperatures of the Pt sites on a 0.64 cm long monolithic Pt/K/Al₂O₃ lean NO_x trap were estimated during CO oxidation, from the conversion of a trace amount of HC and a calibration curve of HC conversion *vs.* temperature. The exhaust stream contained 5% O₂, 10% H₂O, 10% CO₂ and 200 ppm of the HC in N₂. At a base temperature of 300°C with 2% CO, the steady-state Pt temperature was ~130°C higher than the temperature of the exiting exhaust gas.

FUEL CELLS

Fabrication and Performance of Pt/C Electrodes for Low Temperature H₂/O₂ Fuel Cells

T. UMA and M. NOGAMI, *J. Membrane Sci.*, 2007, 302, (1–2), 102–108

Pt/C electrodes (1) were fabricated and their performances compared at low temperature in H₂/O₂ fuel cells with P₂O₅-SiO₂-PWA (phosphotungstic acid) glass membranes. The performance of (1) was investigated at room temperature under humid conditions. A maximum power density of 30 mW cm⁻² and a maximum current density of 121 mA cm⁻² were obtained for (1), with Pt/C loading of 0.15 mg cm⁻² and active area of 0.49 cm², at 30°C and 30% RH.

Composition Effects of FePt Alloy Nanoparticles on the Electro-Oxidation of Formic Acid

W. CHEN, J. KIM, S. SUN and S. CHEN, *Langmuir*, 2007, 23, (22), 11303–11310

The catalytic activities of Fe_xPt_{100-x} nanoparticles (1) in the electrooxidation of HCOOH were evaluated. In chronoamperometric measurements, (1) at $x \approx 50$ showed the highest steady-state current density and had long-term stability. On the basis of the CV studies, the catalytic activity was: Fe₄₂Pt₅₈ > Fe₅₄Pt₄₆ \approx Fe₅₈Pt₄₂ > Fe₁₅Pt₈₅ > Fe₁₀Pt₉₀ > Fe₆₃Pt₃₇. (1) at $x \approx 50$ appeared to exhibit the maximum electrocatalytic activity and stability.

Integrated One-Step PEMFC-Grade Hydrogen Production from Liquid Hydrocarbons Using Pd Membrane Reactor

Y. CHEN, Y. WANG, H. XU and G. XIONG, *Ind. Eng. Chem. Res.*, 2007, 46, (17), 5510–5515

A process of H₂ production was developed by carrying out the reactions during the steam reforming of hydrocarbon fuels and H₂ enrichment in a Pd membrane reactor. A highly H₂-permeable, permselective Pd/modified α -Al₂O₃ composite membrane, and an active catalyst (NiO/La₂O₃/alumina) for steam reforming of both higher hydrocarbons and CH₄ at temperatures lower than 823 K, made one-step H₂ production from steam reforming of liquid hydrocarbons in a membrane reactor feasible.

Carbon-Supported Palladium-Cobalt-Noble Metal (Au, Ag, Pt) Nanocatalysts as Methanol Tolerant Oxygen-Reduction Cathode Materials in DMFCs

J. MATHIYARASU and K. L. N. PHANI, *J. Electrochem. Soc.*, 2007, 154, (11), B1100–B1105

C-supported nanoparticles of Pd-Co-M (M = Pt, Au, Ag) catalysts in a ratio of 70:20:10 were prepared through a reverse microemulsion method. XRD showed well defined reflections corresponding to a f.c.c. phase of Pd. The particle size after heat-treatment (500°C) was \sim 20 nm. Polarisation data indicated Pd-Co-Pt to have better ORR activity than both Pd-Co-Au and Pd-Co-Ag. Pd-Co-Pt also exhibited high MeOH tolerance.

METALLURGY AND MATERIALS

Growing Pt Nanowires as a Densely Packed Array on Metal Gauze

E. P. LEE, Z. PENG, D. M. CATE, H. YANG, C. T. CAMPBELL and Y. XIA, *J. Am. Chem. Soc.*, 2007, 129, (35), 10634–10635

Single-crystal nanowires of Pt <111> have been synthesised on the surface of Pt or W gauze. By reducing the Pt precursor concentration, a layer of nanoparticle agglomerates was eliminated, resulting in a rich surface coverage of Pt nanowires, which nucleate at the defective sites of the substrate. Electrochemical measurements indicated that the active surface area of the Pt nanowire-coated gauze is 2–3 times greater than that of pristine gauze.

IR Spectroscopic Observation of Molecular Transport through Pt@CoO Yolk-Shell Nanostructures

S. KIM, Y. YIN, A. P. ALIVISATOS, G. A. SOMORJAI and J. T. YATES, Jr., *J. Am. Chem. Soc.*, 2007, 129, (30), 9510–9513

FTIR spectroscopy was used to investigate the transport of CO to the Pt cores of Pt@CoO nanoparticles forming CO/Pt species. Pt sites are not present on the outer surfaces of the \sim 10 nm diameter nanostructures, and CO is transported to Pt adsorption sites by an activated surface diffusion process through the CoO shells surrounding \sim 2 nm diameter Pt cores. The onset of the CO diffusion through the CoO shells occurs at \sim 160 K. The CO/CoO species responsible for transport was directly observed at \sim 2147 cm⁻¹.

The Wetting Behavior of NiAl and NiPtAl on Polycrystalline Alumina

A. GAUFFIER, E. SAIZ, A. P. TOMSIA and P. Y. HOU, *J. Mater. Sci.*, 2007, 42, (23), 9524–9528

Sessile drop experiments were performed to investigate the wetting of polycrystalline alumina by NiAl alloys with or without Pt addition ranging from 2.4–10 at.%. Subsequent interfacial morphology was examined using AFM. Pt addition was found to enhance the wettability of NiAl alloys on alumina, reducing the oxide/alloy interface energy and increasing the interfacial mass transport rates.

APPARATUS AND TECHNIQUE

Preparation and Characteristics of Pt/ACC Catalyst for Thermoelectric Thin Film Hydrogen Sensor

J. ZHANG, W. LUAN, H. HUANG, Y. QI and S.-T. TU, *Sens. Actuators B: Chem.*, 2007, 128, (1), 266–272

A thermoelectric (TE) thin film H₂ sensor (1) was composed of a Pt catalyst layer and a TE layer. Activated C fibre cloth was used as the support for the Pt catalyst in (1). The preparation was carried out by an isometric impregnation method. (1) exhibited good sensing properties to H₂ at room temperature with a high temperature difference output (47°C), and quick response and recovery abilities (< 60 s). Good selectivity for H₂ gas was obtained at working temperatures below 160°C.

Novel Nitrite Sensing Using a Palladium-polyphenosafranin Nano-composite

X. ZHU and X. LIN, *Anal. Sci.*, 2007, 23, (8), 981–985

The title nanocomposite was synthesised by electrochemical codeposition at a glassy carbon electrode (GCE) for fabrication of a PPS-Pd/GCE nitrite sensor (1). The PPS-Pd nanocomposite consisted of Pd nanoparticles which stick together due to the polymer, giving a Pd-embedded PPS layer structure. (1) had excellent catalytic activity toward the oxidation of nitrite: high current sensitivity of $0.365 \text{ A/M cm}^{-2}$, good reproducibility, good stability and fast response.

The Influence of Hydrogen Sulfide-to-Hydrogen Partial Pressure Ratio on the Sulfidization of Pd and 70 mol% Pd–Cu Membranes

O. IYOHA, R. ENICK, R. KILLMEYER and B. MORREALE, *J. Membrane Sci.*, 2007, 305, (1–2), 77–92

The behaviour of H_2S -exposed Pd membranes was in agreement with the thermodynamic calculations used in this investigation. Sulfidisation was resisted when exposed to $\text{H}_2\text{S}:\text{H}_2$ ratios below the equilibrium value predicted for Pd₂S formation, and sulfidisation took place when exposed to ratios above the equilibrium values. However, 70 mol% Pd-Cu membranes resisted sulfidisation at some conditions close to the equilibrium values at which sulfidisation was expected, and underwent it at some conditions at which resistance was expected. This is attributed to the Cu segregation at the membrane surface.

CHEMISTRY

Efficient, Ultrafast, Microwave-Assisted Syntheses of Cycloplatinated Complexes

N. GODBERT, T. PUGLIESE, I. AIELLO, A. BELLUSCI, A. CRISPINI and M. GHEDINI, *Eur. J. Inorg. Chem.*, 2007, (32), 5105–5111

Cyclometallated chloridoplatinum complexes containing 2-phenylpyridine, 2-(2'-thienyl)pyridine (1) or 4-methoxypyridine (2), as well as the cyclometallated benzo[*h*]quinoline chlorido complex with 4-methoxypyridine (3), were synthesised in minutes by irradiating the reaction mixture with microwaves. The single-crystal X-ray molecular structures of (1), (2) and (3) are reported.

Design and Preparation of Neutral Substituted Fluorene- and Carbazole-Based Platinum(II)–Acetylde Complexes

J. BATCHA SENECLAUZE, P. RETAILLEAU and R. ZIESSEL, *New J. Chem.*, 2007, 31, (8), 1412–1416

High solubility in apolar or polar solvents of the title complexes was ensured by employing alkyl substituents or a PEG chain grafted on the central fluorene moiety. Further reaction on this fluorene position allowed the construction of a diphenylvinyl group, which extended delocalisation. For the phosphorescent dinuclear complexes, the absorption of the ³MLCT state exhibits a bathochromic shift, which is more pronounced for the carbazole bridging unit.

Pd(SeO₃), Pd(SeO₄), and Pd(Se₂O₅): The First Palladium Oxoselenates

A. ARNDT and M. S. WICKLEDER, *Eur. J. Inorg. Chem.*, 2007, (27), 4335–4339

Depending on the reaction conditions, the reaction of elemental Pd with H_2SeO_4 in sealed glass tubes at 350°C leads to red single crystals of $\text{Pd}(\text{SeO}_3)$ or to yellow-orange single crystals of $\text{Pd}(\text{SeO}_4)$. When SeO_3 is added to the reaction mixture, yellow-orange single crystals of $\text{Pd}(\text{Se}_2\text{O}_5)$ are obtained. The IR spectra show the typical bands for oxoselenate anions.

PHOTOCONVERSION

Luminescent Platinum(II) Complexes Containing Isoquinolinyl Indazolate Ligands: Synthetic Reaction Pathway and Photophysical Properties

S.-Y. CHANG, J. KAVITHA, J.-Y. HUNG, Y. CHI, Y.-M. CHENG, E. Y. LI, P.-T. CHOU, G.-H. LEE and A. J. CARTY, *Inorg. Chem.*, 2007, 46, (17), 7064–7074

$[\text{Pt}(1\text{-iqdzH})\text{Cl}_2]$ (1a) and $[\text{Pt}(3\text{-iqdzH})\text{Cl}_2]$ (1b) (iqdzH = 1- or 3-isoquinolinyl indazole) reacted with excess indazole, sodium picolinate or 3-trifluoromethyl-5-(2-pyridyl) pyrazole [(fppz)H] to afford the respective luminescent complexes $[\text{Pt}(1\text{-iqdz})(\text{L}^{\wedge}\text{X})]$ and $[\text{Pt}(3\text{-iqdz})(\text{L}^{\wedge}\text{X})]$ ($\text{L}^{\wedge}\text{X} = 1\text{-iqdz}$ (2a), 3-*iqdz* (2b), pic (3a, 3b) or fppz (4a, 4b)). For (2), (3) and (4), photoluminescence in degassed CH_2Cl_2 revealed high quantum efficiency and short radiative lifetimes. OLEDs were fabricated using (3a).

Solid-State Luminescence Switching of Platinum(II) Dithioamide Complexes in the Presence of Hydrogen Halide and Amine Gases

F. NASTASI, F. PUNTORIERO, N. PALMERI, S. CAVALLARO, S. CAMPAGNA and S. LANZA, *Chem. Commun.*, 2007, (45), 4740–4742

In the solid state, a non-luminescent Pt(II) dithioamide species, $[\text{Pt}(\text{R}_2\text{-dto})_2]$ (1) (dto = dithioamide; R = butyl), was found to adsorb gaseous HCl, yielding a tight ion pair species which exhibits photoluminescence. The process is quantitatively reversed on heating or by exposing the sample to NH_3 vapours. The luminescence of (1) can be switched on or off by the different gas inputs, yielding gas-activated luminescent molecular logic gates.

SURFACE COATINGS

Vapor Deposition of Ruthenium from an Amidinate Precursor

H. LI, D. B. FARMER, R. G. GORDON, Y. LIN and J. VLASSAK, *J. Electrochem. Soc.*, 2007, 154, (12), D642–D647

Atomic layer deposition and pulsed CVD were employed to deposit Ru thin films (1) from the volatile bis(*N,N'*-di-*tert*-butylacetamidinato)ruthenium(II) dicarbonyl. (1) are fine-grained polycrystalline Ru (< 0.2% impurities). Ru grew as a continuous, electrically conductive, pinhole-free film on WN films. The resistivities of (1) match those of sputtered Ru.