

Abstracts

CATALYSIS – APPLIED AND PHYSICAL ASPECTS

Low Temperature CO Pulse Adsorption for the Determination of Pt Particle Size in a Pt/Cerium-Based Oxide Catalyst

T. Tanabe, Y. Nagai, T. Hirabayashi, N. Takagi, K. Dohmae, N. Takahashi, S. Matsumoto, H. Shinjoh, J. N. Kondo, J. C. Schouten and H. H. Brongersma, *Appl. Catal. A: Gen.*, 2009, **370**, (1–2), 108–113

Large amounts of CO adsorption resulted from a pulse adsorption experiment at 323 K, giving ~300% Pt dispersion in the title catalyst. An *in situ* DRIFTS investigation showed that carbonate species on the Ce oxide surface are responsible for the CO adsorption, as a result of CO spillover. Lowering the temperature to 195 K reduced the amount of CO adsorption. The Pt particle size could be determined by CO pulse adsorption at 195 K.

Preparation and Performance of Ce-Pt-Pd/Stainless Steel Wire Meshes Catalyst

M. Chen, Y. Ma, C. Song, T. Zhang and X. Zheng, *Chin. J. Catal.*, 2009, **30**, (7), 649–653

The title catalyst was prepared by anodic oxidation techniques. The catalyst was characterised by SEM, XPS and O₂ temperature-programmed oxidation. The results indicated that the high catalytic activity and stability of the catalyst are due to the stainless steel wire meshes, whose surface is covered by a porous anodic oxidation membrane. The catalyst showed good catalytic activity for total oxidation of toluene, acetone and ethyl acetate.

Controlled Synthesis of Pompon-Like Self-Assemblies of Pd Nanoparticles under Microwave Irradiation

X. Tong, Y. Zhao, T. Huang, H. Liu and K. Y. Liew, *Appl. Surf. Sci.*, 2009, **255**, (23), 9463–9468

Pd nanoparticles with a uniform, self-assembled pompon-like nanostructure were obtained by decomposition of Pd acetate under microwave irradiation with methyl isobutyl ketone as solvent, in the presence of a small amount of ethylene glycol and KOH. The Pd nano-pompons had average diameters of 28–81 nm and were formed of smaller primary nanoparticles (~2.4 nm). The Pd nano-pompons were easily supported on γ -Al₂O₃ and their catalytic activity for the hydrogenation of cyclohexene was examined.

CATALYSIS – INDUSTRIAL PROCESS

Extending Ru-BINAP Catalyst Life and Separating Products from Catalyst Using Membrane Recycling

D. Nair, H.-T. Wong, S. Han, I. F. J. Vankelecom, L. S. White, A. G. Livingston and A. T. Boam, *Org. Process Res. Dev.*, 2009, **13**, (5), 863–869

Application of organic solvent nanofiltration technology to recycle Ru-BINAP significantly increased the catalyst TON and lifetime for the asymmetric hydrogenation of dimethyl itaconate to dimethyl methylsuccinate (DMMS). By reducing and optimising the catalyst loading (substrate (S):catalyst (C) ratio of 7000), product purities <20 μ g Ru per g DMMS were achieved, and the TON was increased from 6950 (14 reactions at S:C = 500) to 13,100 (2 reactions at S:C = 7000 with no readdition of Ru-BINAP).

EMISSIONS CONTROL

Effect of Hydrocarbon Species on NO Oxidation over Diesel Oxidation Catalysts

K. Irani, W. S. Epling and R. Blint, *Appl. Catal. B: Environ.*, 2009, **92**, (3–4), 422–428

Hydrocarbons were shown to affect NO oxidation over a model Pt-Pd/Al₂O₃ diesel oxidation catalyst. Increasing amounts of propylene resulted in lower NO conversion, due to the consumption of product NO₂ in C₃H₆ oxidation. This was verified by experiments that included NO₂ leading to NO₂ reduction at a significantly lower temperature in the presence of C₃H₆. Furthermore, increasing amounts of C₃H₆ further decreased the NO₂ reduction temperature. Similar results were exhibited with *m*-xylene and dodecane.

The Alteration of the Performance of Field-Aged Pd-Based TWCs Towards CO and C₃H₆ Oxidation

I. Heo, J. W. Choung, P. S. Kim, I.-S. Nam, Y. I. Song, C. B. In and G. K. Yeo, *Appl. Catal. B: Environ.*, 2009, **92**, (1–2), 114–125

The deactivation of the title three-way catalysts (TWCs) for oxidation of CO and C₃H₆ was investigated with respect to the catalyst field mileage by: sweep test (ST), steady-state sweep test and light-off test. No change in the oxidation activity at 673 K towards C₃H₆ was observed, due to the oxidative capability of Pd. The activity towards CO oxidation gradually

decreased with respect to the catalyst mileage by ST. The catalyst deactivation arose from the sintering of Pd and degradation of oxygen storage capacity (OSC). As the deactivation proceeded, the OSC of the TWC simultaneously decreased, due to the degradation of $Ce_xZr_{(1-x)}O_2$ and weakness of the Pd–Ce interaction.

FUEL CELLS

Improving the Activity and Stability of a Pt/C Electrocatalyst for Direct Methanol Fuel Cells

J. Qi, S. Yan, Q. Jiang, Y. Liu and G. Sun, *Carbon*, 2010, **48**, (1), 163–169

Ketjen black (KB) was treated at 900°C in the presence of $Co(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$. The treated KB (TKB) exhibited better graphitisation and a larger mesopore volume than untreated KB. A Pt electrocatalyst supported on TKB was obtained by a modified polyol process. CV and single cell tests showed that the Pt/TKB exhibits better electrochemical activity and stability than Pt/KB.

Bendable Fuel Cells: On-Chip Fuel Cell on a Flexible Polymer Substrate

S. Tominaka, H. Nishizeko, J. Mizuno and T. Osaka, *Energy Environ. Sci.*, 2009, **2**, (10), 1074–1077

On-chip fuel cells on cycloolefin polymer films were successfully fabricated. First, the microchannel was replicated onto a cycloolefin polymer film by hot embossing using a Ni mould. The film was spray coated with a photoresist and then was patterned by UV lithography. The exposed cycloolefin polymer surface was modified with an oxygen plasma treatment; and a 200 µm Au layer with a 30 nm Ti adhesion layer was deposited by electron-beam evaporation. Finally, the Au current collectors were catalysed by electrodeposition of a Pt–Ru alloy for the anode and of a Pd–Co alloy for the cathode.

Facile Synthesis of Nafion-Stabilized Iridium Nanoparticles and Their Direct Use for Fuel Cells and Water Electrolyzers

Y. Zhang, H. Zhang, Y. Zhang, Y. Ma, H. Zhong and H. Ma, *Chem. Commun.*, 2009, (43), 6589–6591

Ir nanoparticles with controlled particle size were prepared using a small amount of Nafion as stabiliser, and a high electrochemically active surface area was obtained. Towards ORR, the Nafion–Ir exhibited comparable activity to Pt, especially when supported on C

black. Towards OER, the activity of Nafion–Ir was higher than that of IrO_2 . After dialysis treatment the Nafion–Ir colloid product could be used to prepare catalyst layers for fuel cells and water electrolyzers.

APPARATUS AND TECHNIQUE

Real-Time Monitoring of Oxidative Burst from Single Plant Protoplasts Using Microelectrochemical Sensors Modified by Platinum Nanoparticles

F. Ai, H. Chen, S.-H. Zhang, S.-Y. Liu, F. Wei, X.-Y. Dong, J.-K. Cheng and W.-H. Huang, *Anal. Chem.*, 2009, **81**, (20), 8453–8458

An electrochemical sensor was fabricated by the electrochemical deposition of Pt nanoparticles on the surface of C fibre microdisc electrodes *via* the nanopores of a Nafion polymer matrix. The Nafion clusters coated on the electrode surface served as the molecular template for the deposition and dispersion of Pt nanoparticles. The sensor demonstrated a high sensitivity for detection of H_2O_2 with a detection limit of 5.0×10^{-9} M. Oxidative bursts from plants play significant roles in plant disease defense and signal transduction. The oxidative burst from individual living plant protoplasts were monitored for the first time in real time.

Free Standing Pt–Au Bimetallic Membranes with a Leaf-Like Nanostructure from Agarose-Mediated Electrodeposition and Oxygen Gas Sensing in Room Temperature Ionic Liquids

X. Shen, X. Chen, J.-H. Liu and X.-J. Huang, *J. Mater. Chem.*, 2009, **19**, (41), 7687–7693

A Pt–Au membrane was electrodeposited onto an agarose-modified ITO substrate, which was then immersed in boiling water to dissolve the agarose. The membrane was carefully separated from the ITO-coated wafer. The free standing membrane was used to prepare an electrode, which was tested by CV measurements. The sharp nanoedges and nanotips on the membrane offer many active centres for catalysis. Sensing behaviour for O_2 in room temperature ionic liquids using the electrode was investigated.

Chiral Separation of Underivatized Amino Acids by Reactive Extraction with Palladium–BINAP Complexes

B. J. V. Verkuijl, A. J. Minnaard, J. G. de Vries and B. L. Feringa, *J. Org. Chem.*, 2009, **74**, (17), 6526–6533

Pd (*S*)-BINAP complexes, $[PdCl_2((S)\text{-BINAP})]$, were employed as hosts in the separation of underivatized

amino acids. The system showed the highest selectivity for the enantioselective liquid–liquid extraction (ELLE) of tryptophan with metal complexes as hosts reported at the time of publication and showed a good selectivity toward a range of natural and unnatural amino acids. The pH, organic solvent and host:substrate ratio are all important parameters in this ELLE. ^{31}P NMR spectroscopy was used to confirm the preferred enantiomer in the extraction experiments. The intrinsic selectivity was deduced by determination of the association constants of $[\text{PdCl}_2((\text{S})\text{-BINAP})]$ with the tryptophan enantiomers.

CHEMISTRY

Behavior of P–Pt and P–Pd Bonds in Phosphido Complexes toward Electrophilic Fragments

E. Alonso, J. Forniés, C. Fortuño, A. Lledós, A. Martín and A. Nova, *Inorg. Chem.*, 2009, **48**, (16), 7679–7690

The reactions between unsaturated 30-valence-electron-count $[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{M}(\text{PPh}_3)]$ ($\text{M} = \text{Pt}, \text{Pd}$) and $[\text{M}'(\text{OCIO}_3)\text{PPh}_3]$ ($\text{M}' = \text{Ag}, \text{Au}$) gave $[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{M}(\text{PPh}_3)(\text{M}'\text{PPh}_3)][\text{ClO}_4]$ ($\text{M} = \text{Pt}, \text{Pd}; \text{M}' = \text{Ag}, \text{Au}$) **1**. The X-ray structures of **1** revealed that the core of the molecules is planar and the Pt–M and M–M' distances indicated the presence of Pt–M and M–M' bonds. A computational study on the formation of **1** and the analysis of the interaction between the binuclear fragment $[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\text{PPh}_3)]$ and the cation $[\text{Ag PPh}_3]^+$ has been carried out on the basis of DFT and showed that the Ag centre interacts weakly with the M and P (PPh₂ ligand) atoms of the binuclear fragment.

Efficient Microwave Syntheses of the Compounds $\text{Os}_3(\text{CO})_{11}\text{L}$, L = NCMe, py, PPh₃

J. Y. Jung, B. S. Newton, M. L. Tonkin, C. B. Powell and G. L. Powell, *J. Organomet. Chem.*, 2009, **694**, (21), 3526–3528

The simple microwave-assisted ligand substitution reactions of triosmium dodecacarbonyl ($\text{Os}_3(\text{CO})_{12}$) were investigated. The activated carbonyl cluster complex $\text{Os}_3(\text{CO})_{11}(\text{NCMe})$ was rapidly prepared in high yield by microwave irradiation of a mixture of $\text{Os}_3(\text{CO})_{12}$ and acetonitrile in a sealed reaction vessel. There was no need for a decarbonylation reagent such as trimethylamine oxide. Microwave irradiation of $\text{Os}_3(\text{CO})_{12}$ in a relatively small amount of acetonitrile was shown to be a useful first step in two-step, one-pot syntheses of the cluster complexes $\text{Os}_3(\text{CO})_{11}(\text{py})$ and $\text{Os}_3(\text{CO})_{11}(\text{PPh}_3)$.

ELECTRICAL AND ELECTRONICS

Effect of Ni Doping on the Microstructure and Magnetic Properties of FePt Films

K. Dong, X. Cheng, J. Yan, W. Cheng, P. Li and X. Yang, *Rare Met.*, 2009, **28**, (3), 257–260

FePtNi films were deposited on glass substrates by RF magnetron sputtering. The as-deposited samples gave $\text{L1}_0\text{-FePtNi}$ films when subjected to vacuum annealing. With increasing Ni content (FePtNi film), the FePt (001) peak position shifts to a higher angle, in comparison with FePt. The perpendicular coercivity decreases from 661 to 142 kA m⁻¹ and magnetisation decreases from 512 to 433 kA m⁻¹ with increasing Ni content. The FePtNi films can effectively reduce the Curie temperature, which makes them promising media candidates in thermally assisted recording.

Self-Assembled CNT Circuits with Ohmic Contacts Using Pd Hexadecanethiolate as In Situ Solder

T. Bhuvana, K. C. Smith, T. S. Fisher and G. U. Kulkarni, *Nanoscale*, 2009, **1**, (2), 271–275

The passive self-assembly and subsequent nanosoldering action of $\text{Pd}(\text{SC}_{16}\text{H}_{35})_2$ was demonstrated on multiwalled C nanotubes (CNTs). $\text{Pd}(\text{SC}_{16}\text{H}_{35})_2$ directs the self-assembly of individual CNTs spanning a gap between Au electrodes. This is achieved by first patterning $\text{Pd}(\text{SC}_{16}\text{H}_{35})_2$ along the edges of the gap electrodes, as it allows direct patterning by electron beam. Thermolysis of $\text{Pd}(\text{SC}_{16}\text{H}_{35})_2$ at 250°C leads to metallisation and ohmic electrical contact between the CNTs and the electrodes beneath.