

Abstracts

CATALYSIS – APPLIED AND PHYSICAL ASPECTS

Controlled Transformation of the Structures of Surface Fe (FeO) and Subsurface Fe on Pt(111)

T. Ma, Q. Fu, Y. Cui, Z. Zhang, Z. Wang, D. Tan and X. Bao, *Chin. J. Catal.*, 2010, **31**, (1), 24–32

Monolayer Fe films deposited on Pt(111) at 487 K were investigated using STM and XPS. The surface composition and structure of Fe/Pt(111) were analysed during stepwise annealing under vacuum. Surface Fe was driven into the subsurface above 800 K, resulting in a Pt-skin surface of Pt/Fe/Pt(111). Oxidation of the Pt-skin structure in O₂ produced a FeO surface structure, FeO/Pt(111). This was transformed into a surface Fe structure by reduction in H₂ at 600 K and into subsurface Fe by further reduction at 800 K. The transformation of surface Fe (FeO) and subsurface Fe in Pt(111) was shown to be reversible in cycled oxidation and reduction. The structures of Fe/Pt(111), Pt/Fe/Pt(111) and FeO/Pt(111) can be transformed one into the other.

Enhanced Catalytic Dehydrogenation of LiBH₄ by Carbon-Supported Pd Nanoparticles

J. Xu, X. Yu, J. Ni, Z. Zou, Z. Li and H. Yang, *Dalton Trans.*, 2009, (39), 8386–8391

Thermal dehydrogenation of LiBH₄ was shown to be improved in the presence of Pd nanoparticle/C catalysts, even at very low catalyst concentration. Smaller Pd nanoparticles resulted in greater enhancement of the catalytic dehydrogenation than did larger Pd nanoparticles. A reversible hydrogenation/dehydrogenation with a H₂ capacity of ~4.3 wt% was observed.

Nano-Scale Bi-Layer Pd/Ta, Pd/Nb, Pd/Ti and Pd/Fe Catalysts for Hydrogen Sorption in Magnesium Thin Films

X. Tan, C. T. Harrower, B. Shalchi Amirkhiz and D. Mitlin, *Int. J. Hydrogen Energy*, 2009, **34**, (18), 7741–7748

The elevated temperature (250°C) volumetric H₂ sorption behaviour of Mg thin films catalysed by the title catalysts was investigated. Sorption of H₂ by Mg catalysed by Pd was determined and used as the baseline. Sorption cycling demonstrated that with Pd and Pd/Fe the sorption kinetics of the Mg films rapidly degraded. However with Pd/Nb, Pd/Ti and Pd/Ta

the composite remained cycleable. After multiple sorption cycles Pd/Nb and Pd/Ti had the fastest kinetics. NbH_{0.5} and TiH₂ were formed during testing and identified by XRD.

CATALYSIS – REACTIONS

Palladium Complexes with Aqueous-Partitioning Dibenzylideneacetone Ligands. A New Strategy for Catalyst Design in Suzuki Polycondensation Reactions

J. W. Eddy, E. A. Davey, R. D. Malsom, A. R. Ehle, S. Kassel and F. E. Goodson, *Macromolecules*, 2009, **42**, (22), 8611–8614

Pd–dibenzylideneacetone (Pd–dba) catalyst precursors with water-solubilising substituents have been developed, which yielded molecular weights in a Suzuki polycondensation that were superior to those obtained with traditional catalyst systems. The polycondensations were carried out in CH₂Cl₂/H₂O in the presence of K₃PO₄. While their performance still did not match that of bis[tri(*o*-tolyl)phosphine]palladium(0), these Pd–dba complexes are claimed to offer advantages in terms of atmospheric stability and handling convenience.

Catalytic Activity of Ruthenium Nanoparticles Supported on Carbon Nanotubes for Hydrogenation of Soybean Oil

S. Guo, K. Y. Liew and J. Li, *J. Am. Oil Chem. Soc.*, 2009, **86**, (12), 1141–1147

Ru nanoparticle/MWCNT catalysts with various Ru loadings (1 wt%, 3 wt% and 5 wt%) were prepared by reduction with H₂ or NaBH₄ for selective hydrogenation of soybean oil at 338 K and initial pressure of 1.066 MPa. These catalysts were characterised using TEM, XRD, N₂ adsorption–desorption and H₂-TPD techniques. The Ru particles were dispersed more homogeneously on the surface of the MWCNTs after being reduced with H₂. The catalysts with 3 wt% and 5 wt% Ru loadings had higher hydrogenation activity. The NaBH₄-reduced catalyst had higher *cis*-isomer selectivity.

Adsorption and Desorption of SO_x on Diesel Oxidation Catalysts

O. Kröcher, M. Widmer, M. Elsener and D. Rothe, *Ind. Eng. Chem. Res.*, 2009, **48**, (22), 9847–9857

The deactivation of NO oxidation by SO₂ was investigated using commercial DOCs coated on cordierite

monolith; with Pt/Al₂O₃ as a reference material. The maximum NO conversion for the fresh DOCs was 38% at 350°C. Under typical exhaust gas conditions (1 ppm SO₂, 250°C), the DOCs functioned as sulfur traps. The SO_x storage involved a fast saturation of the catalyst surface with H₂SO₄, which hampered NO conversion, and a slow, long-lasting sulfation of the washcoat. The storage capacities of the DOCs reached their maxima at 250°C. Adsorbed H₂SO₄ desorbed between 350°C and 400°C, whereas more stable compounds, such as Al₂(SO₄)₃, decomposed at higher temperatures. Deactivated DOCs could be regenerated at >350°C. Repeated or longer thermal treatments resulted in a reduced sulfur storage capacity and irreversible activity losses for NO oxidation due to sintering.

Lean NO_x Reduction by Hydrogen over Pt-Supported Rare Earth Oxide Catalysts and Their In Situ DRIFTS Study

M. Itoh, K. Motoki, M. Saito, J. Iwamoto and K. Machida, *Bull. Chem. Soc. Jap.*, 2009, **82**, (9), 1197–1202

Pt supported on CeO₂, Pr₆O₁₁, Eu₂O₃ and Gd₂O₃ catalysts were prepared and their NO_x SCR characteristics using H₂ were studied under 10 vol% excess O₂. Only Pt/CeO₂ exhibited good NO conversion (~80%) with ~40% N₂ selectivity. The other catalysts showed little NO_x reduction activity due to the high solid basicity of their supports. *In situ* DRIFTS measurements for NO_x reduction on Pt/CeO₂ showed the presence of NO₃⁻ species, indicating that the reduction proceeds *via* formation of this nitrate.

Improved Activity of Rh/CeO₂-ZrO₂ Three-Way Catalyst by High-Temperature Ageing

M. Haneda, O. Houshito, T. Sato, H. Takagi, K. Shinoda, Y. Nakahara, K. Hiroe and H. Hamada, *Catal. Commun.*, 2010, **11**, (5), 317–321

The TWC 0.4 wt% Rh/CeO₂-ZrO₂ was prepared by impregnation of CeO₂-ZrO₂ (with different Ce:Zr molar ratios) with a Rh(III) nitrate solution, followed by drying and calcination at 600°C for 5 h in air. High-temperature ageing of the catalysts was generally carried out by oscillatory change of the reaction gas composition between stoichiometric and lean at 1000°C for 25 h. The effect of ageing on the activity of Rh/CeO₂-ZrO₂ for the NO-C₃H₆-O₂ reaction was dependent on the Ce:Zr molar ratio. The activity of Rh/CeO₂-ZrO₂ with a Ce:Zr molar ratio of 74:26 was significantly enhanced by the ageing, due to the for-

mation and stabilisation of active reduced Rh species and a change in the surface properties of CeO₂-ZrO₂ which inhibited the formation of formate species that would poison the catalytically active sites.

FUEL CELLS

Direct Glucose Fuel Cell: Noble Metal Catalyst Anode Polymer Electrolyte Membrane Fuel Cell with Glucose Fuel

C. A. Appleby, D. Ingersoll, S. Sarangapani, M. Kelly and P. Atanassov, *J. Electrochem. Soc.*, 2010, **157**, (1), B86–B89

A 1 cm² constant flow glucose-O₂ fuel cell was prepared based on Pt-RuO₂ anode catalysts and Pt cathode catalysts. Operation at various glucose concentrations revealed the presence of a region of the polarisation curve in which additional polarisation led to a decrease in current rather than the expected increase. The appearance of this polarisation loss is proposed to be due to the adsorption of byproduct lactones to the Pt-RuO₂ surface.

Synthesis and Characterization of Pd-Ni Nanoalloy Electrocatalysts for Oxygen Reduction Reaction in Fuel Cells

J. Zhao, A. Sarkar and A. Manthiram, *Electrochim. Acta*, 2010, **55**, (5), 1756–1765

Pd-Ni nanoalloy/C electrocatalysts, with different Pd:Ni atomic ratios, were synthesised using a modified polyol method, followed by heat treatment in 10% H₂-90% Ar atmosphere at 500–900°C. Electrochemical studies showed that Pd₈₀Ni₂₀ heated at 500°C had the highest mass catalytic activity for the ORR, with stability and catalytic activity significantly higher than found with Pd. The Pd-Ni electrocatalysts exhibited higher MeOH tolerance than Pt.

METALLURGY AND MATERIALS

Nanoporous Au-Pt Alloys As Large Strain Electrochemical Actuators

H.-J. Jin, X.-L. Wang, S. Parida, K. Wang, M. Seo and J. Weissmüller, *Nano Lett.*, 2010, **10**, (1), 187–194

(Au_{1-x}Pt_x)₂₅Ag₇₅ alloys **1** were prepared by inductive melting ($x = 0.1$ and 0.2) or repeated arc melting ($x = 0.5$). The alloys were annealed at 950°C for >72 h and then quenched in water. Nanoporous Au_{1-x}Pt_x alloys were formed by dealloying **1** in 1 M HClO₄ solution, using a pseudo Ag/AgCl reference electrode. Uniform and fine nanoporous structures were formed with no

indication of bulk phase separation. Dilatometry experiments demonstrated electrochemical actuation with a large reversible strain amplitude.

BIOMEDICAL AND DENTAL

Effect of CaCl₂ Hydrothermal Treatment on the Bone Bond Strength and Osteoconductivity of Ti–0.5Pt and Ti–6Al–4V–0.5Pt Alloy Implants

M. Nakagawa and J. Yamazoe, *J. Mater. Sci.: Mater. Med.*, 2009, **20**, (11), 2295–2303

Ti–0.5Pt and Ti–6Al–4V–0.5Pt alloys were hydrothermally treated (HT-treated) at 200°C in 10 mmol l⁻¹ CaCl₂ solution for 24 h. Histological investigations of the HT-treated materials were carried out using Wistar strain rats (SD rats). The specimens were implanted in the tibia of SD rats. To measure the bone bond strengths, a pull-out test was conducted. From the early postoperative stages, direct bone contact was obtained for the HT-treated implants. Within 1–4 weeks of implantation, the bone contact ratios and bone bond strengths of the HT-treated implants were higher than those of the non-treated implants.

Platinum(II) Compounds Bearing Bone-Targeting Group: Synthesis, Crystal Structure and Antitumor Activity

Z. Xue, M. Lin, J. Zhu, J. Zhang, Y. Li and Z. Guo, *Chem. Commun.*, 2010, **46**, (8), 1212–1214

Soluble mononuclear Pt compounds (**1–4**) in which the non-leaving groups are linked with ‘bone-seeking’

bisphosphonate tetraethyl esters were synthesised. X-Ray crystallography was used to determine the crystal structures of **2** and **3**. In cytotoxicity assay against human osteosarcoma (MG-63) and ovarian cancer (COC1) cell lines, **2** and **4** demonstrated much higher activity than **1** and **3**, which is correlated to the length of the linkers between the chelating moiety and the bisphosphonate esters. An apoptotic assay of **4**, the compound with highest activity, was conducted, and showed a different mode of cell death compared to cisplatin. The circular dichroism and electrophoretic mobility studies revealed that **1–4** hardly bind to DNA.

ELECTROCHEMISTRY

The Electrochemical Recovery of Metallic Palladium from Spent Electroless Plating Solution

N. Warner and M. L. Free, *JOM*, 2009, **61**, (10), 27–30

Semiconductor bond pads can be coated with Pd for good electrical properties and wire adhesion. The Pd is deposited by immersing the wafers in an electroless Pd plating solution. The remaining Pd in depleted spent plating solution can be recovered by electrochemical deposition onto a high surface area cathode. The recovery of the Pd improves the sustainability of the process.

SURFACE COATINGS

Investigation on the Oxidation Behavior of Mo–Ru Hard Coatings

Y.-I. Chen, *Surf. Coat. Technol.*, 2009, **204**, (6–7), 860–864

Mo–Ru coatings can be used as protective coatings on the top surface of glass moulding dies. The moulding atmosphere consists of steadily purged N₂ and residual O₂. The diffusion of O₂ into Mo_{38.1}Ru_{61.9} coatings annealed at 600°C in an O₂-containing atmosphere was investigated. Solid solution strengthening and recrystallisation due to the introduction of O₂ increased the surface hardness of the coatings from 13 GPa to 19 GPa after 4 h. An oxide scale and a Mo-depleted zone were formed after 8 h, due to the preferential oxidation of Mo and high volatility of MoO₃. Cracks on the surface and in the Mo-depleted zone were observed after 20 h.

