

ABSTRACTS

CATALYSIS – APPLIED AND PHYSICAL ASPECTS

FT-IR Investigation of NO_x Storage Properties of Pt–Mg(Al)O and Pt/Cu–Mg(Al)O Catalysts Obtained from Hydrotalcite Compounds

S. MORANDI, F. PRINETTO, G. GHIOTTI, M. LIVI and A. VACCARI, *Microporous Mesoporous Mater.*, 2008, 107, (1–2), 31–38

The NO_x storage capability upon admission of NO and NO₂ with or without excess O₂ at ≤ 623 K was investigated by *in situ* FT-IR for the title catalysts. Pure NO₂ is adsorbed by a dismutation reaction with simultaneous formation of nitrates and nitrites that evolve to nitrates (“dismutation route”); nitrite evolution is promoted by the metal phase. When metal phase is present, the nitrites’ oxidation is further accelerated by O₂. When O₂ is present, NO is stored by: (a) oxidation to nitrites followed by their oxidation to nitrates; or (b) oxidation to NO₂, followed by the “dismutation route”. (a) and (b) are promoted by the metal phases.

Complete Oxidation of Methane over Palladium Supported on Alumina Modified with Calcium, Lanthanum, and Cerium Ions

B. STASINSKA, W. GAC, T. IOANNIDES and A. MACHOCKI, *J. Nat. Gas Chem.*, 2007, 16, (4), 342–348

The supports for Pd/Al₂O₃ and Pd/(Al₂O₃ + MO_x) (M = Ca, La, Ce) were prepared by a sol-gel method. They were dried either conventionally or with sc-CO₂, and then impregnated with Pd nitrate solution. The introduction of Ca, La or Ce oxide caused a decrease of the surface area, dependent on the support precursor drying method. These modifiers decreased the activity of the Pd catalysts for CH₄ oxidation. Improvement of the Pd activity by La and Ce support modifier was observed only at low temperatures.

Carbon Microsphere Supported Pd Catalysts for the Hydrogenation of Ethylene

K. C. MONDAL, L. M. CELE, M. J. WITCOMB and N. J. COVILLE, *Catal. Commun.*, 2008, 9, (4), 494–498

C microspheres were prepared from acetylene at 800°C. The microspheres were loaded with 2% Pd, both before and after H₂SO₄/HNO₃ acid treatment. The acid-treated C microsphere-supported Pd catalyst exhibited better ethylene hydrogenation activity.

Selective Oxidation of Styrene to Acetophenone over Supported Au–Pd Catalyst with Hydrogen Peroxide in Supercritical Carbon Dioxide

X. WANG, N. S. VENKATARAMANAN, H. KAWANAMI and Y. IKUSHIMA, *Green Chem.*, 2007, 9, (12), 1352–1355

Selective oxidation of styrene to acetophenone was carried out over supported Pd–Au catalysts with H₂O₂ in sc-CO₂. The Al₂O₃ support showed the best catalytic performance. The presence of the sc-CO₂ improved the oxidation of styrene to acetophenone and inhibited the formation of byproducts.

CATALYSIS – REACTIONS

Stille Cross-Coupling Reaction Using Pd/BaSO₄ as Catalyst Reservoir

A. V. COELHO, A. L. F. DE SOUZA, P. G. DE LIMA, J. L. WARDELL and O. A. C. ANTUNES, *Appl. Organomet. Chem.*, 2008, 22, (1), 39–42

Stille cross-couplings of iodobenzene and tributylphenyltin were achieved in EtOH/H₂O using different amounts of Pd/BaSO₄ as catalyst reservoir in a ligand-free system. The catalyst was reused up to three times with some loss in activity. Filtration of the catalyst and product extraction gave a solution that kept its activity, indicating that Pd(0)/Pd(II) are the catalytic species.

α-Arylation of Ketones Using Highly Active, Air-Stable (DtBPF)PdX₂ (X = Cl, Br) Catalysts

G. A. GRASA and T. J. COLACOT, *Org. Lett.*, 2007, 9, (26), 5489–5492

α-Arylation of ketones with aryl chlorides and bromides using (DtBPF)PdX₂ (X = Cl, Br) catalysts gave 80–100% yield of the coupled products under relatively mild conditions at low catalyst loadings. The X-ray structure determination of (DtBPF)PdCl₂ revealed the largest P–Pd–P bite angle (104.2°) for a ferrocenyl bisphosphine ligand. ³¹P NMR monitoring of the (DtBPF)PdCl₂-catalysed reaction of 4-chlorotoluene with propiophenone indicated that the DtBPF remained coordinated in a bidentate mode.

C–C Coupling Reaction of Triphenylbismuth(V) Derivatives and Olefins in the Presence of Palladium Nanoparticles Immobilized in Spherical Polyelectrolyte Brushes

Y. B. MALYSHEVA, A. V. GUSHCHIN, Y. MEI, Y. LU, M. BALLAUFF, S. PROCH and R. KEMPE, *Eur. J. Inorg. Chem.*, 2008, (3), 379–383

C–C couplings were carried out at 50°C using Ph₃BiX₂ (X = O₂CH, O₂CMe, O₂CEt, O₂C^tPr, O₂C^tBu, O₂CⁿBu, O₂CPh, O₂CCH₂Cl, O₂CCl₃, O₂CCF₃) and a range of olefins in the presence of Pd nanoparticles immobilised in spherical polyelectrolyte brushes (Pd@SPB). Ph₃Bi(O₂CCF₃)₂ was the most active. This route allows the formation of Heck-type products without the addition of base. A very low Pd loading was used.

Ruthenium-Based NHC-Arene Systems as Ring-Opening Metathesis Polymerisation Catalysts

N. LEDOUX, B. ALLAERT and F. VERPOORT, *Eur. J. Inorg. Chem.*, 2007, (35), 5578–5583

The coordination of the standard NHC ligand H₂IMes to [(*p*-cymene)RuCl₂]₂ was established to be unattainable, so bidentate NHC analogues were synthesised instead. These analogues are *O*-hydroxyaryl-substituted NHCs, capable of binding with the metal centre through the O atom as well as through the carbene C atom. Their chelating properties improved the stability of the corresponding Ru arene complexes.

FUEL CELLS

Synergistic Effect of CeO₂ Modified Pt/C Electrocatalysts on the Performance of PEM Fuel Cells

H. XU and X. HOU, *Int. J. Hydrogen Energy*, 2007, 32, (17), 4397–4401

Pt/C electrocatalysts were modified by CeO₂ with sol-gel and dipping processes. TEM and CV results showed that some Pt active surfaces were covered by CeO₂, the electrochemical surface area of modified Pt/C was less than that of the unmodified one, and the sol-gel process covered less electrocatalyst surface area than the dipping process. Using modified Pt/C as a cathode electrocatalyst enhanced performance.

Synthesis and Characterization of Electrodeposited Ni–Pd Alloy Electrodes for Methanol Oxidation

K. S. KUMAR, P. HARIDOSS and S. K. SESHADRI, *Surf. Coat. Technol.*, 2008, 202, (9), 1764–1770

A wide compositional range of Ni–Pd alloy electrocatalysts (1) were prepared by electrodeposition for use as anode materials for DMFCs in alkaline conditions. As-plated (1) were nanocrystalline, single phase, f.c.c. materials, indicating the formation of a complete solid solution in the alloy. Compositional analysis of the alloys indicated that the Pd composition increased with decrease in current density. (1) were active for MeOH oxidation in alkaline medium.

Pd–Co Carbon-Nitride Electrocatalysts for Polymer Electrolyte Fuel Cells

V. DI NOTO, E. NEGRO, S. LAVINA, S. GROSS and G. PACE, *Electrochim. Acta*, 2007, 53, (4), 1604–1617

Two groups of materials with the formula K_n[Pd_xCo_yC_zN_mH_m] were synthesised with: (a) molar ratio $y:x > 1$; and (b) molar ratio $y:x < 1$. Vibrational studies revealed that (a) and (b) systems consisted of two polymorphs of α - and graphitic-like CN nanomaterials. The electrochemical performance of the Pd–Co–CNs of (a) obtained at $t_f \geq 700^\circ\text{C}$ was higher than that measured for a Pt-based commercial electrocatalyst in terms of both activity towards the O reduction and H oxidation reactions; also the resistance towards poisoning by MeOH.

METALLURGY AND MATERIALS

Infrared Spectroscopy of Physisorbed and Chemisorbed N₂ in the Pt(111)(3×3)N₂ Structure

K. GUSTAFSSON, G. S. KARLBERG and S. ANDERSSON, *J. Chem. Phys.*, 2007, 127, (19), 194708 (6 pages)

The adsorption of N₂, at 30 K, on Pt(111) and Pt(111)(1×1)H surfaces was investigated using IR spectroscopy and LEED. The IR spectra revealed that N₂ exclusively physisorbed on the Pt(111)(1×1)H surface, whereas both physisorbed and chemisorbed N₂ were detected on the Pt(111) surface. Physisorbed N₂ was the majority species in the latter case, and the two adsorption states showed an almost identical uptake behaviour, which indicates that they are intrinsic constituents of the growing (3×3) N₂ islands.

Synthesis of Colloidal Particles of Poly(2-vinylpyridine)-Coated Palladium and Platinum in Organic Solutions under the High Temperatures and High Pressures

M. HARADA, M. UEJI and Y. KIMURA, *Colloids Surf. A: Physicochem. Eng. Aspects*, 2008, 315, (1–3), 304–310

Colloidal dispersions of PVP-coated Pd and Pt particles in toluene/1-propanol were synthesised by the decomposition and reduction of Pd(acac)₂ and Pt(acac)₂ respectively under high-temperature and high-pressure conditions. At 473 K and 25 MPa, colloidal dispersions ([Pd] = 7.5 mM) of Pd particles of average diameter 1.9 nm with narrow particle size distributions, were synthesised within seconds. Pt particles (average diameter of 2.1 nm) were also obtained.

Synthesis of Palladium Nanowire Arrays with Controlled Diameter and Length

G. KARTOPU, S. HABOUTI and M. ES-SOUNI, *Mater. Chem. Phys.*, 2008, 107, (2–3), 226–230

Pd nanowire (NW) arrays were synthesised using porous alumina templates and direct current electrodeposition. The electrolyte was K₂PdCl₄ in H₂SO₄. Final pore sizes of the alumina templates were ~ 65 and 35 nm. A high filling rate (> 90%) was obtained using 65 μm thick templates. The NWs synthesised in 65 nm pores were polycrystalline and textured, but those in 35 nm pores were single crystalline. The alumina template was dissolved away, leaving self-standing NWs supported on a conductive thin film.

Creep Deformation Mechanisms in Ru–Ni–Al Ternary B2 Alloys

F. CAO and T. M. POLLOCK, *Metall. Mater. Trans. A*, 2008, 39, (1), 39–49

The creep behaviour of five Ru–Ni–Al alloys with compositions across the ternary RuAl–NiAl B2 phase field was studied within the range 1223–1323 K. These alloys exhibited exceptional creep strength compared to other high melting temperature intermetallics. A continuous increase of the melting temperature and creep resistance with increasing Ru:Ni ratio was observed.

APPARATUS AND TECHNIQUE

Temperature-Independent Ceria- and Pt-Doped Nano-Size TiO₂ Oxygen Lambda Sensor Using Pt/SiO₂ Catalytic Filter

F. HAGHIGHAT, A. KHODADADI and Y. MORTAZAVI, *Sens. Actuators B: Chem.*, 2008, 129, (1), 47–52

The overlap of TiO₂-based O₂ sensor responses in the rich and lean regions was eliminated by using a 1.0 wt.% Pt/SiO₂ catalytic filter (1) located in front of the sensors. Nanosized TiO₂ was prepared by a microemulsion method and then doped with 1.0 wt.% Pt and 10.0 wt.% CeO₂ by an impregnation method. The sensor was exposed to synthetic exhaust gases with λ values in the range 0.8–1.4. All of the sensors showed low-high transitions at about $\lambda = 1.0$. By using (1) only CO or O₂ reaches the sensors.

Electrochemical DNA Biosensors Based on Palladium Nanoparticles Combined with Carbon Nanotubes

Z. CHANG, H. FAN, K. ZHAO, M. CHEN, P. HE and Y. FANG, *Electroanalysis*, 2008, 20, (2), 131–136

MWCNTs and Pd nanoparticles were dispersed in Nafion, and used to modify a GCE. Oligonucleotides with amino groups at the 5' end were covalently linked to carboxylic groups of MWCNTs on the electrode. The hybridisation events were monitored by differential pulse voltammetry using methylene blue as an indicator. The detection limit of the method for target DNA was 1.2×10^{-13} M.

Hydrogen Permeation of Thin, Free-Standing Pd/Ag23% Membranes Before and After Heat Treatment in Air

A. L. MEJDELL, H. KLETTE, A. RAMACHANDRAN, A. BORG and R. BREDESEN, *J. Membrane Sci.*, 2008, 307, (1), 96–104

The title membranes (thicknesses ~ 1.3 – 5.0 μm) were produced by magnetron sputtering. Thermal treatment in air at 300°C significantly enhanced their H_2 flux. The permeability values became fairly similar after treatment, indicating bulk diffusion was the main rate-limiting step for H_2 flux. The effect on permeation was found to depend on the membrane thickness, with less enhancement for the ~ 5.0 μm thick membranes. The treated samples had higher surface roughness, larger surface area and larger surface grains.

BIOMEDICAL AND DENTAL

On the Hydrolysis Mechanism of the Second-Generation Anticancer Drug Carboplatin

M. PAVELKA, M. F. A. LUCAS and N. RUSSO, *Chem. Eur. J.*, 2007, 13, (36), 10108–10116

The hydrolysis reaction mechanisms of carboplatin were investigated by combining DFT with the conductor-like dielectric continuum model (CPCM) approach. The theoretical calculations on carboplatin were used to obtain energy profiles and optimised structures for the rate-limiting process in its neutral hydrolysis. The results indicated that if carboplatin undergoes a hydration process, it should be doubly hydrated prior to reaction with DNA.

CHEMISTRY

Double Complex Salts of Pt and Pd Amines with Zn and Ni Oxalates – Promising Precursors of Nanosized Alloys

A. V. ZADESENETS, E. YU. FILATOV, K. V. YUSENKO, YU. V. SHUBIN, S. V. KORENEV and I. A. BAIDINA, *Inorg. Chim. Acta*, 2008, 361, (1), 199–207

$[\text{M}(\text{NH}_3)_4][\text{M}'(\text{Ox})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Pd}, \text{Pt}$; $\text{M}' = \text{Ni}, \text{Zn}$) were synthesised from solutions containing $[\text{M}(\text{NH}_3)_4]^{2+}$ and $[\text{M}'(\text{Ox})_2(\text{H}_2\text{O})_2]^{2-}$. Thermal decomposition of the prepared salts in He or H_2 atmosphere at 200 – 400°C resulted in formation of nanosized bimetallic powders with crystallite sizes 50 – 250 Å.

PHOTOCONVERSION

Aggregation-Induced Phosphorescent Emission (AIPE) of Iridium(III) Complexes

Q. ZHAO, L. LI, F. LI, M. YU, Z. LIU, T. YI and C. HUANG, *Chem. Commun.*, 2008, (6), 685–687

An AIPE was observed for $\text{Ir}(\text{ppy})_2(\text{DBM})$ and $\text{Ir}(\text{ppy})_2(\text{SB})$ ($\text{DBM} = 1,3$ -diphenyl-1,3-propanedione, $\text{SB} = 2$ -(naphthalen-1-yliminomethyl)phenol). These Ir(III) complexes, in powder form, exhibited moderately intense emissions. Furthermore, addition of non-solvent H_2O into dilute MeCN solutions can turn on their photoluminescent emission.

Ultrafast Luminescence in $\text{Ir}(\text{ppy})_3$

G. J. HEDLEY, A. RUSECKAS and I. D. W. SAMUEL, *Chem. Phys. Lett.*, 2008, 450, (4–6), 292–296

For $\text{Ir}(\text{ppy})_3$, an emission with a lifetime component of 230 fs in the spectral region 500 – 560 nm is assigned to the population equilibration between electronic sub-states of the lowest excited triplet state, with energy dissipation by intramolecular vibrational redistribution. At shorter wavelengths a strong emission with a faster decay was observed, which is attributed to a state with a higher admixture of singlet character. A slower decay on a 3 ps timescale is attributed to vibrational cooling.

SURFACE COATINGS

Platinum OMCVD Processes and Precursor Chemistry

C. THURIER and P. DOPPELT, *Coord. Chem. Rev.*, 2008, 252, (1–2), 155–169

Organometallic chemical vapour deposition (OMCVD) allows the formation of Pt thin films as a fine dispersion of Pt particles. Pt precursors having good volatility and a good thermal stability window are available. The best systems are MeCpPtMe_3 and EtCpPtMe_3 , the latter being O_2 - and H_2O -stable at ambient temperature. $(\text{cod})\text{Pt}(\text{Me})_2$ is less volatile but it is easily synthesised in high yield. These precursors benefit from facile decomposition under the CVD conditions. Decomposition is rapid in the presence of $\text{O}_2(g)$ or $\text{H}_2(g)$. Films can be obtained with only traces of impurities, C being the most common. (97 Refs.)

Electrochemical Formation of Ir Oxide/Polyaniline Composite Films

H. ELZANOWSKA, E. MIASEK and V. I. BIRSS, *Electrochim. Acta*, 2008, 53, (6), 2706–2715

IrOx/PANI composite films were made by forming an anodic IrOx film on bulk Ir and then depositing PANI into its pores. All of the PANI film that was electrochemically active was in direct electrical contact with the Ir surface at the base of the IrOx film pores. Thin films of Ir nanoparticles, subsequently converted to IrOx , were also used as a template for PANI formation within the porous structure. These hybrid films exhibited an enhanced internal porosity, high charge densities, unusual electrochromic behaviour, and very rapid charge transfer kinetics.