

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Study of an Internally-Oxidized Pd_{0.97}Ce_{0.03} Alloy

V. M. AZAMBUJA, D. S. DOS SANTOS, L. PONTONNIER, M. MORALES and D. FRUCHART, *Scr. Mater.*, 2006, 54, (10), 1779–1783

Cold-worked foils of Pd_{0.97}Ce_{0.03} underwent an internal oxidation heat treatment at 1073 K for 72 h. TEM showed the precipitation of needle-shaped CeO₂ (1) with a cubic lattice parameter of 5.4 Å. (1) exhibited preferential growth directions relative to the Pd matrix which correspond to the diagonal of the Pd cube. (1) were ~ 20–40 nm wide and 1–2 μm long, in coherence with the Pd matrix.

X-ray Photoelectron Spectroscopy and Magnetism of Mn–Pd Alloys

M. COLDEA, M. NEUMANN, S. G. CHIUZBAIAN, V. POP, L. G. PASCUT, O. ISNARD, A. F. TAKÁCS and R. PACURARIU, *J. Alloys Compd.*, 2006, 417, (1–2), 7–12

Mn_xPd_{1-x} alloys and compounds (1) were prepared by Ar arc melting. The samples were melted repeatedly (four times) in the same atmosphere to ensure homogeneity. The electronic structures of (1) were studied using XPS. Both valence band and core level spectra were analysed. The magnetic properties of (1) are strongly correlated with their crystallographic properties and can be explained considering only the near-neighbour antiferromagnetic interactions between both Mn and Pd atoms and Mn–Mn pairs.

Dramatic Evolution of Magnetic Properties Induced by Electronic Change in Ce(Pd_{1-x}Ag_x)₂Al₃

P. SUN, Q. LU, T. IKENO, T. KUWAI, T. MIZUSHIMA and Y. ISIKAWA, *J. Phys.: Condens. Matter*, 2006, 18, (24), 5715–5723

Measurements of lattice parameters (*a*, *b*), magnetic susceptibility $\chi(T)$ and magnetisation *M(H)*, specific heat *C(T)*, and electrical resistivity $\rho(T)$ were made for Ce(Pd_{1-x}Ag_x)₂Al₃. It was found that with increasing *x* the system varies from antiferromagnetism to ferromagnetism at *x* ~ 0.05, then back at *x* ~ 0.45. The magnetic evolution resembles that of Ce(Pd_{1-x}Cu_x)₂Al₃.

CHEMICAL COMPOUNDS

Protonation of Platinum(II) Dialkyl Complexes Containing Ligands with Proximate H-Bonding Substituents

G. J. P. BRITOVSEK, R. A. TAYLOR, G. J. SUNLEY, D. J. LAW and A. J. P. WHITE, *Organometallics*, 2006, 25, (8), 2074–2079

Pt(II) dimethyl complexes [Pt(L)Me₂], L = unsymmetrically substituted bipyridine, were prepared. Reactions in MeCN with 1 equiv. of a strong acid gave [Pt(L)Me(CH₃CN)]⁺. The selectivity of the protonation reactions is reported to be governed by steric effects rather than H-bonding effects.

Synthesis and Structure of NbPdSi

M. VALLDOR and R. PÖTTGEN, *Z. Naturforsch.*, 2006, 61b, (3), 339–341

NbPdSi (1) was prepared by melting the elements in an arc furnace. Well-shaped single crystals of (1) were obtained by annealing in an induction furnace. The Pd and Si atoms were shown by powder and single crystal XRD analysis to build up a 3D [PdSi] network where each Pd atom has a strongly distorted tetrahedral Si coordination at Pd–Si of 242–250 pm. The Nb atoms fill channels left in the [PdSi] network.

N-Heterocyclic Carbenes: Synthesis, Structures, and Electronic Ligand Properties

W. A. HERRMANN, J. SCHÜTZ, G. D. FREY and E. HERDTWECK, *Organometallics*, 2006, 25, (10), 2437–2448

Rh(COD)X(NHC) complexes were synthesised. The relative σ -donor/ π -acceptor quality of various NHC ligands was classified by means of IR spectroscopy at the corresponding Rh(CO)₂I(NHC). Single crystal XRD studies of Rh pyrazolin- and tetrazolinylidene complexes are reported. Different azolium salts were applied to obtain Rh and Ir complexes with two and four carbene ligands.

Bis[iridium(I)] Complex of Inverted N-Confused Porphyrin

M. TOGANO, H. KONAGAWA and H. FURUTA, *Inorg. Chem.*, 2006, 45, (10), 3852–3854

When a N-confused tetraphenylporphyrin was treated with 2.0 equiv. of IrCl(CO)₂(*p*-toluidine) and 10 equiv. of NaOAc in toluene/THF = 20/1 (v/v) at 100°C for 3.5 h, a novel bis[iridium(I)] complex (1), wherein the confused pyrrole ring took an inverted conformation, was obtained in 17% yield. The reactions were significantly accelerated by THF. (1) can be handled in air without special care. No decomposition was observed by heating in 1,2-Cl₂C₆H₄. No demetallation occurred on CF₃COOH addition.

Fullerene Polypyridine Ligands: Synthesis, Ruthenium Complexes, and Electrochemical and Photophysical Properties

Z. ZHOU, G. H. SAROVA, S. ZHANG, Z. OU, F. T. TAT, K. M. KADISH, L. ECHEGOYEN, D. M. GULDI, D. I. SCHUSTER and S. R. WILSON, *Chem. Eur. J.*, 2006, 12, (16), 4241–4248

Fullerene coordination ligands (1) with a single bpy or tpy unit were synthesised. Coordination of (1) to Ru(II) gave linear rod-like donor-acceptor systems. Steady-state fluorescence of [Ru(bpy)₂(bpy-C₆₀)]²⁺ showed a rapid solvent-dependent, intramolecular quenching of the Ru(II) MLCT excited state. Electrochemical studies on [Ru(bpy)₂(bpy-C₆₀)]²⁺ and [Ru(tpy)(tpy-C₆₀)]²⁺ indicated electronic coupling between the Ru centre and the fullerene core.

ELECTROCHEMISTRY

Chemical and Electrochemical Synthesis of Polyaniline/Platinum Composites

J. M. KINYANJUI, N. R. WIJERATNE, J. HANKS and D. W. HATCHETT, *Electrochim. Acta*, 2006, 51, (14), 2825–2835

The direct chemical synthesis of Pt-polyaniline (1) composites was achieved by the oxidation of aniline by PtCl_6^{2-} . The Pt particles were $\sim 1 \mu\text{m}$ in diameter. Electrochemical synthesis of (1) was initiated by the uptake and reduction of PtCl_6^{2-} into an *a priori* electrochemically deposited polyaniline film. This method produced a uniform dispersion of Pt particles with diameters of 200 nm–1 μm .

Electrocatalytic Activity for Hydrogen Evolution of Polypyrrole Films Modified with Noble Metal Particles

M. TRUEBA, S. P. TRASATTI and S. TRASATTI, *Mater. Chem. Phys.*, 2006, 98, (1), 165–171

Polypyrrole (Ppy) films with Pt, Ru and Ir particles were electrosynthesised on the surface of austenitic stainless steel by: (a) electrodeposition of a polymer film from a solution already containing an anionic metal complex, followed by potentiodynamic or galvanostatic reduction; or (b) presynthesised Ppy films modified by galvanostatic electrodeposition of the metals from solutions of their metal complexes. The electrocatalytic activity of the modified electrodes for the H_2 evolution reaction was tested in H_2SO_4 (0.05 M) by potentiodynamic techniques (0.5 mV s^{-1}).

PHOTOCONVERSION

Platinum–Acetylde Polymer Based Solar Cells: Involvement of the Triplet State for Energy Conversion

F. GUO, Y.-G. KIM, J. R. REYNOLDS and K. S. SCHANZE, *Chem. Commun.*, 2006, (17), 1887–1889

Blends of a blue-violet absorbing Pt-acetylde polymer (1) with 1-(3-(methoxycarbonyl)propyl)-1-phenyl[6.6]C₆₁ (PCBM), can be used as the active material in a photovoltaic device. (1) acts as the chromophore and electron donor blended with PCBM as an electron acceptor. Photoinduced charge separation in the blends is believed to occur *via* the triplet excited state of the organometallic polymer.

Structurally Integrated Organic Light Emitting Diode-Based Sensors for Gas Phase and Dissolved Oxygen

R. SHINAR, Z. ZHOU, B. CHOUDHURY and J. SHINA, *Anal. Chim. Acta*, 2006, 568, (1–2), 190–199

The O_2 -sensitive dyes Pt- or Pd-octaethylporphyrin (1), were embedded in polystyrene, or dissolved in solution. Their performance was compared to that of $\text{Ru}(\text{dpp})_3^{2+}$. A green OLED, based on Alq_3 , was used to excite (1). The O_2 level was monitored in the gas phase and in H_2O , EtOH and toluene by measuring changes in the PL lifetime τ of (1).

Photophysical Properties of the Photosensitizer $[\text{Ru}(\text{bpy})_2(5\text{-CNphen})]^{2+}$ and Intramolecular Quenching by Complexation of Cu(II)

M. G. MELLACE, F. FAGALDE, N. E. KATZ, H. R. HESTER and R. SCHMEHL, *J. Photochem. Photobiol. A: Chem.*, 2006, 181, (1), 28–32

The lifetime of the $^3\text{MLCT}$ emitting state of $[\text{Ru}(\text{bpy})_2(5\text{-CNphen})]^{2+}$ has been determined in MeCN by flash photolysis and time correlated single photon counting techniques. The value obtained, $\tau = 2.2 \mu\text{s}$, suggests its potential use as a photosensitiser in molecular devices. Static and dynamic quenching of the complex luminescence by Cu^{2+} ions was seen.

ELECTRODEPOSITION AND SURFACE COATINGS

Adhesion and Bonding of Pt/Ni and Pt/Co

Overlayers: Density Functional Calculations

G. F. CABEZA, N. J. CASTELLANI and P. LÉGARÉ, *J. Phys. Chem. Solids*, 2006, 67, (4), 690–697

The electronic and energetic properties of Pt/Ni and Pt/Co surfaces are examined using the full-potential linearised augmented plane wave method. The results of the shifts in the d-band centers when one metal (Pt) is pseudomorphically deposited on another with smaller lattice constant (Ni, Co) are presented, together with those corresponding to the surface and adhesion energies. The results for pure Ni, Co and Pt surfaces are given to compare with data in the literature.

Self-Assembled Palladium Nanowires by Electroless Deposition

Z. SHI, S. WU and J. A. SZPUNAR, *Nanotechnology*, 2006, 17, (9), 2161–2166

The self-assembly production of Pd nanowires (1) has been carried out by electroless deposition on a porous stainless steel template. Various arrays of self-assembled (1) in the form of single wire, parallel and curved wires, intersections and network structures are obtainable. (1) can be built in a self-assembled manner by the assembly of nanoparticles generated in the initial stages of the deposition without any external field except the chemical reaction.

Selective Growth of IrO_2 Nanorods Using Metalorganic Chemical Vapor Deposition

G. WANG, D.-S. TSAI, Y.-S. HUANG, A. KOROTCOV, W.-C. YEH and D. SUSANTI, *J. Mater. Chem.*, 2006, 16, (8), 780–786

Area-selective growth of IrO_2 nanorods (1) was achieved via MOCVD using $(\text{MeCp})\text{Ir}(\text{COD})$ on a sapphire (012) or (100) substrate which consisted of patterned SiO_2 as the nongrowth surface. Orientation of (1) was controlled by the in-plane epitaxial relation between the IrO_2 crystal and sapphire, along with the IrO_2 growth habit in the [001] direction. The photolithography method gave better resolution in preserving rod orientation of (1) at the growth and nongrowth boundary zone.

APPARATUS AND TECHNIQUE

High-Purity CO_x-Free H₂ Generation from NH₃ via the Ultra Permeable and Highly Selective Pd Membranes

J. ZHANG, H. XU and W. LI, *J. Membrane Sci.*, 2006, 277, (1–2), 85–93

A compact H₂ generation system combining NH₃ decomposition with separation by a series of Pd membranes (3 μm) has been developed to provide high-purity, CO_x-free H₂ for fuel cell applications. Removal of H₂ product in a Pd membrane reactor was shown to promote NH₃ conversion over a Ni-based catalyst. However, *ex situ* integration, in which an NH₃ cracker was followed by a Pd membrane purifier, was deemed more suitable for practical uses due to its high productivity of pure H₂.

Nanocomposite of Pd-Polyaniline as a Selective Methanol Sensor

A. A. ATHAWALE, S. V. BHAGWAT and P. P. KATRE, *Sens. Actuators B: Chem.*, 2006, 114, (1), 263–267

A Pd-polyaniline nanocomposite (1) was synthesised by oxidative polymerisation of an aniline solution containing Pd nanoparticles. (1) was highly selective and sensitive to MeOH vapours. The selectivity of (1) was further investigated by exposing it to MeOH-EtOH and MeOH-isopropanol. Here (1) exhibited a response identical to that for pure MeOH, except for the response time.

Hydrogen Permeation Characteristics of Thin Pd Membrane Prepared by Microfabrication Technology

Y. ZHANG, J. GWAK, Y. MURAKOSHI, T. IKEHARA, R. MAEDA and C. NISHIMURA, *J. Membrane Sci.*, 2006, 277, (1–2), 203–209

A Pd membrane (1), ~ 2.5 μm thick, on Si wafer was successfully prepared using microfabrication technology. H₂ permeability of (1) was investigated within 473–673 K, and found to be ~ 50–65% that of a 0.70 mm thick Pd membrane. Grain growth was found in (1) after permeation, and the presence of CO₂ reduced H₂ permeability significantly.

HETEROGENEOUS CATALYSIS

Effect of Pt Precursors on Catalytic Activity of Pt/TiO₂ (Rutile) for Water Gas Shift Reaction at Low-Temperature

H. IIDA, K. KONDO and A. IGARASHI, *Catal. Commun.*, 2006, 7, (4), 240–244

Pt/TiO₂ (rutile) catalysts for the low temperature-WGSR were prepared from various Pt precursors. The catalytic activity decreases for the precursors used: H₂PtCl₆·6H₂O, Pt(C₃H₇O₂)₂ > [Pt(NH₃)₄]Cl₂ > [Pt(NH₃)₄](NO₃)₂ > *cis*-[Pt(NO₂)₂(NH₃)₂]. There was a linear relationship between catalytic activity and Pt dispersion. The TOF for the LT-WGSR was almost constant regardless of Pt dispersion.

Enhancement of Naphthalene Hydrogenation over PtPd/SiO₂-Al₂O₃ Catalyst Modified by Gold

B. PAWELEC, V. LA PAROLA, S. THOMAS and J. L. G. FIERRO, *J. Mol. Catal. A: Chem.*, 2006, 253, (1–2), 30–43

The effect of the support (amorphous silica-alumina (ASA) and C multiwall nanotubes (MWNTs)) on the activity of PtPd catalysts in naphthalene hydrogenation is described. Also, the effect of Au incorporation on PtPd/ASA was studied. AuPtPd/ASA showed the highest naphthalene conversion and lowest deactivation. The less acidic PtPd/C MWNTs did not show S-resistance. The contribution of the acid sites of the support to S-resistance and their deactivation by coke are discussed.

Improved CO Oxidation in the Presence and Absence of Hydrogen over Cluster-Derived PtFe/SiO₂ Catalysts

A. SIANI, B. CAPTAIN, O. S. ALEXEEV, E. STAFYLA, A. B. HUNGRIA, P. A. MIDGLEY, J. M. THOMAS, R. D. ADAMS and M. D. AMIRIDIS, *Langmuir*, 2006, 22, (11), 5160–5167

Pt₅Fe₂/SiO₂ and PtFe₂/SiO₂ samples (1), prepared from organometallic cluster precursors decarbonylated in H₂ at 350°C, were found to be highly active for the oxidation of CO in the presence or absence of H₂. Pt-Fe nanoparticles were formed with sizes of 1–2 nm. A higher degree of dispersion and more homogeneous mixing of the metals were observed in (1) as compared to a conventionally impregnation prepared PtFe/SiO₂ (2). (1) were also more active than Pt/SiO₂ or (2) for the oxidation of CO in air.

Hydrogenation of Sunflower Oil on Pd Catalysts in Supercritical Conditions: Effect of the Particle Size

C. M. PIQUERAS, M. B. FERNÁNDEZ, G. M. TONETTO, S. BOTTINI and D. E. DAMIANI, *Catal. Commun.*, 2006, 7, (6), 344–347

Sunflower oil hydrogenation was carried out using supercritical propane and Pd/γ-Al₂O₃. The selectivity to *cis*-isomers and the production of saturated fatty acids was favoured by a small Pd particle size (< 2 nm). There was no significant variation in the reaction rate nor in the TOF. Despite the fact that during the reaction a phase separation occurred, propane was in supercritical state in both phases.

Effects of Natural Water Ions and Humic Acid on Catalytic Nitrate Reduction Kinetics Using an Alumina Supported Pd-Cu Catalyst

B. P. CHAPLIN, E. ROUNDY, K. A. GUY, J. R. SHAPLEY and C. J. WERTH, *Environ. Sci. Technol.*, 2006, 40, (9), 3075–3081

The NO₃⁻ reduction rate of a H₂O sample using Pd-Cu/γ-Al₂O₃ was 2.4 × 10⁻⁰¹ l/min g cat. The addition of SO₄²⁻, SO₃²⁻, HS⁻, Cl⁻, HCO₃⁻, OH⁻ and humic acid decreased the NO₃⁻ reduction rate. Preferential adsorption of Cl⁻ inhibited NO₃⁻ reduction to a greater extent than NO₂⁻ reduction. Dissolved constituents in groundwater decreased the NO₃⁻ reduction rate. Removal of dissolved organic matter using activated C increased the NO₃⁻ reduction rate.

HOMOGENEOUS CATALYSIS

Recovery and Reuse of Ionic Liquids and Palladium Catalyst for Suzuki Reactions Using Organic Solvent Nanofiltration

H. WONG, C. J. PINK, F. C. FERREIRA and A. G. LIVINGSTON, *Green Chem.*, 2006, 8, (4), 373–379

Organic solvent nanofiltration was used for separating ionic liquids (1) and the catalyst $\text{Pd}_2(\text{dba})_3\text{-CHCl}_3$ from Suzuki cross-couplings. The reactions were carried out in 50:50 wt.% ethyl acetate and (1). The post reaction mixture was diluted further with ethyl acetate and then separated by nanofiltration. The product was recovered in the nanofiltration permeate, while (1) and Pd catalyst were retained by the membrane.

Unexpected Roles of Molecular Sieves in Palladium-Catalyzed Aerobic Alcohol Oxidation

B. A. STEINHOFF, A. E. KING and S. S. STAHL, *J. Org. Chem.*, 2006, 71, (5), 1861–1868

The effect of molecular sieves (MS3A) on $\text{Pd}(\text{OAc})_2/\text{pyridine}$ (1) and $\text{Pd}(\text{OAc})_2/\text{DMSO}$ (2) was investigated by performing kinetic studies of alcohol oxidation. MS3A enhanced the rate of (1)-catalysed oxidation of alcohols. This was attributed to the ability of MS3A to serve as a Brønsted base. In contrast, no rate enhancement was observed with (2). Both (1) and (2) exhibit improved catalyst stability in the presence of MS3A, resulting in higher catalytic TONs. The MS3A provided a heterogeneous surface that hinders bulk aggregation of Pd metal.

Unsymmetric-1,3-Disubstituted Imidazolium Salt for Palladium-Catalyzed Suzuki-Miyaura Cross-Coupling Reactions of Aryl Bromides

H.-W. YU, J.-C. SHI, H. ZHANG, P.-Y. YANG, X.-P. WANG and Z.-L. JIN, *J. Mol. Catal. A: Chem.*, 2006, 250, (1–2), 15–19

Unsymmetric 1,3-disubstituted-imidazolium salts (1) derived from ferrocene were prepared, and their preliminary activities as precursors of N-heterocyclic carbene ligands for Pd-catalysed cross-coupling of aryl bromides with phenylboronic acid were studied. A combination of $\text{Pd}(\text{OAc})_2$ and (1) was an excellent catalyst system for the Suzuki-Miyaura cross-coupling of aryl bromides with phenylboronic acid in the presence of Cs_2CO_3 .

Rh(0) Nanoparticles as Catalyst Precursors for the Solventless Hydroformylation of Olefins

A. J. BRUSS, M. A. GELESKY, G. MACHADO and J. DUPONT, *J. Mol. Catal. A: Chem.*, 2006, 252, (1–2), 212–218

The hydroformylation of 1-alkenes can be performed in solventless conditions, using ligand-modified or unmodified Rh(0) nanoparticles (1) prepared in imidazolium ionic liquids as catalyst precursors. Aldehydes were generated when 5.0 nm (1) are used. With smaller nanoparticles, chemoselectivity is decreased; large sized nanoparticles (15 nm) produce only small amounts of aldehydes, similarly to a classical heterogeneous Rh/C catalyst precursor.

FUEL CELLS

Thermal Stability in Air of Pt/C Catalysts and PEM Fuel Cell Catalyst Layers

O. A. BATURINA, S. R. AUBUCHON and K. J. WYNNE, *Chem. Mater.*, 2006, 18, (6), 1498–1504

The thermal stability of Pt/Vulcan XC 72 and a 46 wt.% Pt/Vulcan XC 72/Nafion layer was studied. Low temperature (100–200°C) C combustion occurred in the presence of Pt. In PEMFC catalyst layers, the thermal decomposition temperature of Nafion is lowered by ~ 100°C to 300°C in the presence of Pt/C.

High Performance PtRuIr Catalysts Supported on Carbon Nanotubes for the Anodic Oxidation of Methanol

S. LIAO, K.-A. HOLMES, H. TSAPRAILIS and V. I. BIRSS, *J. Am. Chem. Soc.*, 2006, 128, (11), 3504–3505

PtRuIr/C MWNTs system (1) was prepared using an organic colloid synthesis method. (1) has a very high real surface area and is highly active toward the oxidation of MeOH. The Ir component acts as a promoter. The splitting of the Pt(111) XRD feature into four peaks and the shift to larger d spacing reflect the high dispersion of the metallic components.

ELECTRICAL AND ELECTRONIC ENGINEERING

Interface Effect on Ferroelectricity at the Nanoscale

C.-G. DUAN, R. F. SABIRIANOV, W.-N. MEI, S. S. JASWAL and E. Y. TSYMBAL, *Nano Lett.*, 2006, 6, (3), 483–487

A first-principles study of ultrathin KNbO_3 ferroelectric films (1) placed between two metal electrodes, either Pt or SrRuO_3 , was carried out. The strength of bonding and intrinsic dipole moments at the interfaces was shown to control the ferroelectricity. The polarisation profile was inhomogeneous across the film thickness. The critical thickness for the net polarisation of (1) was predicted to be ~ 1 nm for Pt and 1.8 nm for SrRuO_3 electrodes.

Calculations and Measurements of Contact Resistance of Semi-Transparent Ni/Pd Contacts to p-GaN

K. H. A. BOGART and J. CROFTON, *J. Electron. Mater.*, 2006, 35, (4), 605–612

Calculations of specific contact resistance (1) as a function of doping and barrier height were performed for p-GaN. (1) were measured for oxidised Ni/Au, Pd, and oxidised Ni/Pd ohmic contact metal schemes to p-GaN. The Ni/Pd contact had the lowest (1). Some Ni had diffused away from the GaN surface to the contact surface, with the bulk of the Pd located in between two areas of Ni. Both Ni and Pd interdiffused with the GaN at the semiconductor surface. The majority of the O was as NiO. Predominantly NiO and PdO species were formed, with higher Ni and Pd oxides at the contact surface.