

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Surface Oxides and their Effect on the Oxidation Behavior of Amorphous and Nanoquasicrystalline Zr-Pd and Zr-Pt Alloys

K. MONDAL, U. K. CHATTERJEE and B. S. MURTY, *J. Mater. Res.*, 2006, 21, (3), 639–646

The oxidation of melt-spun $Zr_{80}Pt_{20}$ (1) and $Zr_{75}Pd_{25}$ (2) with a nanoquasicrystalline phase embedded in an amorphous matrix has been investigated isothermally as well as nonisothermally in static air. XRD and SEM were used to study the oxides formed. For (1), the kinetics of oxidation is sluggish compared to (2), which is due to the strong interaction between Zr and Pt atoms.

Determination of Hydrogen Absorption Isotherm and Diffusion Coefficient in $Pd_{81}Pt_{19}$ Alloy

F. VIGIER, R. JURCZAKOWSKI and A. LASIA, *J. Electroanal. Chem.*, 2006, 588, (1), 32–43

Permeation and impedance techniques (1) were used to study H absorption into $Pd_{81}Pt_{19}$ foil. The total amount of H absorbed is smaller than in pure Pd, and the absorption plateau is obtained at negative overpotentials. The H diffusion coefficient was determined by various (1). (1) gave similar values with the exception of the small differential step permeation technique and electrochemical impedance spectroscopy in the transmissive mode. H-induced stress might cause the deviations observed.

Thermodynamic Assessment of the Hf–Os System

C. GUO and Z. DU, *J. Alloys Compd.*, 2006, 407, (1–2), 188–192

The Hf–Os system was assessed by the CALPHAD technique. A three-sublattice model $(Hf, Os)_{0.5}(Hf, Os)_{0.5}Va_3$ was applied to the intermediate B2 compound $HfOs$. Using this model, the ordered B2 and the disordered Hf-rich b.c.c. phases are described by a single Gibbs energy function. The intermetallic compound $HfOs_2$ was treated as $(Hf, Os)(Hf, Os)_2$ by a two-sublattice model with Hf and Os on the first and second sublattices, respectively.

CHEMICAL COMPOUNDS

Mono- and Di-nuclear Platinum(II) Complexes Containing O- and N-Bonded Acetamide

E. J. ZIOLKOWSKI, P. TURNER and L. M. RENDINA, *Inorg. Chem. Commun.*, 2006, 9, (1), 53–56

The preparation and interconversion reactions of novel O- and N-bonded acetamide and deprotonated N- and N,O-bonded acetamide derivatives of Pt(II)-terpy are reported. $[Pt(MeCN)(terpy)](OTf)_2$ was used as the precursor for the O-acetamide derivative. The X-ray structures of the mononuclear N-acetamido and dinuclear N,O-acetamido species were determined.

Synthesis and Characterization of the Nitrides of Platinum and Iridium

J. C. CROWHURST, A. F. GONCHAROV, B. SADIGH, C. L. EVANS, P. G. MORRALL, J. L. FERREIRA and A. J. NELSON, *Science*, 2006, 311, (5765), 1275–1278

High-pressure and high-temperature synthesised Pt nitride (1) of stoichiometry PtN_2 has a large bulk modulus. A structure that is isostructural with pyrite was proposed for (1). A recoverable nitride of Ir (2) was also synthesised under similar conditions. Although (2) has the same stoichiometry as (1), (2) exhibits much lower structural symmetry. The bulk modulus of (2) is also very large.

Novel Acyclic Carbene-Substituted Phospha-Palladacycles

G. D. FREY and W. A. HERRMANN, *J. Organomet. Chem.*, 2005, 690, (24–25), 5876–5880

The synthesis of a phospha-palladacycle substituted with an acyclic carbene, without reduction of the Pd(II) complex, has been achieved for the first time. The reaction of bis(dialkyl)aminocarbenes with the very stable phospha-palladacycles leads to metastable η^1 -carbene complexes. The latter can be converted by intramolecular reduction to Pd(0) complexes.

Tetrazolecalix[4]arenes as New Ligands for Palladium(II)

V. BOYKO, R. RODIK, O. DANYLYUK, L. TSYMBAL, Y. LAMPEKA, K. SUWINSKA, J. LIPKOWSKI and V. KALCHENKO, *Tetrahedron*, 2005, 61, (52), 12282–12287

The synthesis of bis- and tetrakis-tetrazole derivatives of a calix[4]arene (1) and the structural characterisation of a calixarene containing 4 tetrazole groups at the upper end of a macrocycle and its complex with $PdCl_2$ were carried out. The tetrazole ligating groups are at the upper rim of (1) to give (1) their bowl shape. (1) can be used in self-assembled cage structures having transition metal cations as linkers.

PHOTOCONVERSION

Synthesis and pH-Sensitive Luminescence of Bis-terpyridyl Iridium(III) Complexes Incorporating Pendent Pyridyl Groups

K. J. ARM, W. LESLIE and J. A. G. WILLIAMS, *Inorg. Chim. Acta*, 2006, 359, (4), 1222–1232

Three new series of pyridyl-appended bis-terpyridyl Ir complexes (1) are luminescent at room temperature, with long luminescence lifetimes in the μs range in air-equilibrated aqueous solution. The emission intensity and lifetimes of (1) are sensitive to the protonation state of the pyridyl group. Emission may be either quenched or augmented according to the structure of the ligand in (1).

A New Family of Ruthenium(II) Polypyridine Complexes Bearing 5-Aryltetrazolate Ligands as Systems for Electrochemiluminescent Devices

S. STAGNI, A. PALAZZI, S. ZACCHINI, B. BALLARIN, C. BRUNO, M. MARCACCIO, F. PAOLUCCI, M. MONARI, M. CARANO and A. J. BARD, *Inorg. Chem.*, 2006, 45, (2), 695–709

Mono- and dinuclear Ru polypyridyls containing 5-aryltetrazolates were prepared. Spectroscopic studies of the uncoordinated tetrazolate ligand and complexes highlighted good luminescence efficiency and poor bridge-mediated electronic communication between the metal centres of the dinuclear complexes (1). For one of (1), a very high ECL efficiency was observed.

SURFACE COATINGS

Effect of Thermally Grown Oxide (TGO) Microstructure on the Durability of TBCs with PtNiAl Diffusion Bond Coats

I. SPITSBERG and K. MORE, *Mater. Sci. Eng. A*, 2006, 417, (1–2), 322–333

The effect of preoxidation surface treatments on Pt-modified NiAl bond coats and electron beam deposited thermal barrier coatings (TBCs) has been studied. The formation of a surface oxide having a coarse-grained columnar structure during the preoxidation process enhanced the TBC performance. Increased TBC durability was consistent with a slower oxide growth rate during exposure of the TBC to high-temperature, cyclic conditions. An oxide microstructure having fewer grain boundaries was achieved by preoxidising the bond coat prior to TBC deposition at an intermediate partial pressure of O₂.

Processing TiPdNi Base Thin-Film Shape Memory Alloys Using Ion Beam Assisted Deposition

E. BALDWIN, B. THOMAS, J. W. LEE and A. RABIEI, *Surf. Coat. Technol.*, 2005, 200, (7), 2571–2579

Thin films of TiPdNi (1) were processed using ion beam assisted deposition (IBAD). As-deposited (1) were found to be amorphous. Postdeposition annealing caused decohesion and delamination. IBAD with *in situ* heat treatment gave fully martensitic films 1.5 μm thick and with reduced grain size and film defects. (1) can be used in MEMS microactuator applications.

APPARATUS AND TECHNIQUE

Self-Aligned Platinum-Silicide Nanowires for Biomolecule Sensing

F.-H. KO, Z.-H. YE, C.-C. CHEN and T.-F. LIU, *J. Vac. Sci. Technol. B*, 2005, 23, (6), 3000–3005

The immobilisation of a single-stranded capture DNA onto a Pt-silicide 40 nm nanowire (1) was verified by a fluorescence-labelling technique. A field-effect transistor can distinguish the complementary, mismatched, and denatured DNA *via* the conductance difference. (1) can sense the minimal target DNA concentration down to 100 fM, and the signal is still 1000-fold larger than the noise signal.

Pd/Porous-GaAs Schottky Contact for Hydrogen Sensing Application

A. SALEHI, A. NIKFARJAM and D. J. KALANTARI, *Sens. Actuators B: Chem.*, 2006, 113, (1), 419–427

Pd/GaAs (1) and Pd/porous-GaAs (2) Schottky diode sensors were fabricated and characterised using forward and reverse *I-V* measurements in response to H₂ at different temperatures. (1) exhibited low sensitivity to H₂. The detection limit of (1) was improved by poring the GaAs wafer using electrochemical HF etching, followed by depositing a Pd layer on its surface to give (2). (2) exhibited sensitivity three times that of (1), with a response time of 1 s for 500 ppm H₂.

The Electroanalytical Detection of Hydrazine: A Comparison of the Use of Palladium Nanoparticles Supported on Boron-Doped Diamond and Palladium Plated BDD Microdisc Array

C. BATCHELOR-MCAULEY, C. E. BANKS, A. O. SIMM, T. G. J. JONES and R. G. COMPTON, *Analyst*, 2006, 131, (1), 106–110

Both a random distribution of Pd nanoparticles supported on a B-doped diamond (BDD) electrode (1) and a Pd plated BDD microelectrode array (2) provide a sensing platform for the electrocatalytic detection of hydrazine. (1) has a sensitivity and limit of detection of 60 mA mol⁻¹ L and 2.6 μM, while (2) gives 8 mA mol⁻¹ L and 1.8 μM, respectively. The random Pd distribution in (1) leads to clumps of Pd nanoparticles that effectively act as microelectrodes.

HETEROGENEOUS CATALYSIS

NO_x Storage and Reduction on Pt/Alumina Catalysts: Effects of Alkaline-Earth and Rare-Earth Metal Additives

H.-Y. LIN, C.-J. WU and Y.-W. CHEN, *Ind. Eng. Chem. Res.*, 2006, 45, (1), 134–141

Pt/Al₂O₃ catalysts (1), modified with alkaline-earth or rare-earth metal oxides, were prepared by incipient-wetness impregnation. The performance and durability of NO_x storage of (1) were studied under a lean-burn/rich-burn cycle process. The Ba-promoted (1) had better storage capability and duration, while the Ce-promoted (1) had a higher NO storage capability. (1) containing both Ba and Ce demonstrated high NO storage/conversion. The best operating temperature range was 350–400°C.

The Influence of Fuel Type on Carbon Deposition over Precious Metal Containing Motorcycle Catalysts

L. JIA, J. ZHANG, M. SHEN, J. WANG and M. LIN, *Catal. Commun.*, 2005, 6, (12), 757–761

The influence of fuel type on C deposition over Pt and Pd containing motorcycle catalysts was studied. MTBE blended gasoline gave carbonaceous species in the form of C_xH_y, whereas for blended EtOH fuel the species are C_xH₂O. The majority of the carbonaceous species are deposited on the Pt and Pd sites. FTIR confirmed aromatic rings, alkyl groups and their partial oxidation products in the C deposits.

Washcoating Method for Pd/ γ -Al₂O₃ Deposition on Metallic Foams

L. GIANI, C. CRISTIANI, G. GROPPi and E. TRONCONI, *Appl. Catal. B: Environ.*, 2006, 62, (1–2), 121–131

A method (1) for coating open celled metal foams with a Pd-Al₂O₃ thin layer (20 μ m thick) was developed. A sol-gel of pseudoboehmite as a precursor of γ -Al₂O₃ was used to fill the porous structure by percolation. This was activated with Pd using wet impregnation. In an alternative method (2), dry impregnation of γ -Al₂O₃ with Pd was performed and a slurry was prepared (+ H₂O/HNO₃). The slurry was deposited by percolation through the foam structure. Both (1) and (2) produced highly active foams, resulting in light-off temperatures for catalytic CO oxidation of 175–250°C. CO conversions with (1) were > (2), indicating (1) gave more uniform coating.

Hydrogenation of Plant Sterols over a Polymer Fiber-Supported Pd Catalyst

J. HELMINEN, E. PAATERO and U. HOTANEN, *Org. Process Res. Dev.*, 2006, 10, (1), 51–63

The hydrogenation of a wood-based plant sterol mixture, β -sitosterol, β -sitostanol, campesterol and campestanol, was investigated using a Pd/poly(acrylic acid) grafted polyethylene fibre catalyst (1). Metal species were not leached into the reaction mixture, and mechanical agitation did not damage (1). The scale-up of the hydrogenation process was successfully carried out in pilot-plant and industrial reactors.

Catalytic Autoignition of Higher Alkane Partial Oxidation on Rh-Coated Foams

K. A. WILLIAMS and L. D. SCHMIDT, *Appl. Catal. A: Gen.*, 2006, 299, 30–45

Steady-state production of syngas (CO and H₂) was attained within 5 s after admitting large alkanes and air into a short-contact-time reactor by using an automotive fuel injector and initially preheating the Rh-coated foam catalysts (1) above the respective catalytic autoignition temperature for each fuel. Minimum catalytic autoignition temperatures on (1) were \sim 260°C for *n*-octane and 240°C for *i*-octane and *n*-decane. In contrast, catalytic autoignition of *n*-hexadecane indirectly occurred at > 220°C because exothermic homogeneous chemistry had preheated (1) by 30–60°C to \sim 280°C.

HOMOGENEOUS CATALYSIS

Palladium-Catalyzed Addition of Alkynes to Cyclopropenes

J. YIN and J. D. CHISHOLM, *Chem. Commun.*, 2006, (6), 632–634

Pd(OAc)₂/[(Me)₃PH]BF₄/Et₃N was investigated for the addition of 4-pentyn-1-ol to 3,3-diphenylcyclopropene. The cyclopropane ring remained intact to provide an alkynylcyclopropane. The active Pd-phosphine complex is generated *in situ*. Coupling of alkynes and cyclopropenes can thus be used for synthesis of alkynylcyclopropanes under mild conditions.

Industrial-Scale Palladium-Catalyzed Coupling of Aryl Halides and Amines – A Personal Account

S. L. BUCHWALD, C. MAUGER, G. MIGNANI and U. SCHOLZ, *Adv. Synth. Catal.*, 2006, 348, (1–2), 23–39

The Pd-catalysed coupling of amines and aryl halides or aryl alcohol derivatives has progressed from a laboratory small-scale transformation into a general, efficient and robust reaction over the last ten years. Applications of this method from an industrial viewpoint, including phosphane ligand synthesis and synthesis of arylpiperazines, arylhydrazines and diarylamines, are described. The issues of scale-up and safety are included. (33 Refs.)

Environmentally Friendly Synthesis of Biaryls: Suzuki Reaction of Aryl Bromides in Water at Low Catalyst Loadings

N. JIANG and A. J. RAGAUSKAS, *Tetrahedron Lett.*, 2006, 47, (2), 197–200

Pd(DPPF)Cl₂ has been shown to be an extremely active catalyst for the Suzuki coupling reaction of aryl bromides in H₂O. This procedure gave biaryls in excellent yields and high TONs (TONs \leq 870,000 for the reaction of 1-bromo-4-nitrobenzene and phenylboronic acid). A 20% aqueous PEG-2000 solution as the reaction media allows this catalytic system to be readily recyclable for three runs.

Simple and Economical Conversion of Organic Compounds with H₂O₂ Catalyzed by Ruthenium (III) Chloride

P. K. TANDON, R. BABOO, A. K. SINGH and GAYATRI, *Appl. Organomet. Chem.*, 2006, 20, (1), 20–23

Aromatic aldehydes, hydrocarbons, cyclohexanol and benzyl alcohol, dissolved in acetic acid, were oxidised in quantitative to moderate yields by 50% H₂O₂ in the presence of traces of RuCl₃ (1) (\sim 10⁻⁸ mol). Conditions for highest yields were obtained. Higher concentrations of (1) decreased the yield. Oxidation in the aromatic aldehydes was selective at the aldehydic group only, and other groups remained unaffected. The extent of oxidation in phenanthrene depends on temperature or the relative amount of substrate or both. It is proposed that the oxocentred carboxylate species of Ru(III) catalyses the oxidation.

A Simple and Practical Phase-Separation Approach to the Recycling of a Homogeneous Metathesis Catalyst

A. MICHROWSKA, L. GULAJSKI and K. GRELA, *Chem. Commun.*, 2006, (8), 841–843

An efficient new strategy for homogeneous Ru-catalyst phase-separation and recovery which provides products of excellent purity with low Ru content has been designed. An asarone-derived Ru carbene olefin metathesis catalyst (1) exhibited high reactivity and was easily separated after reaction by deposition on silica gel. (1) was reused up to nine times without needing fluororous solvents or special silica gel.

Bifunctional Transition Metal-Based Molecular Catalysts for Asymmetric Syntheses

T. IKARIYA, K. MURATA and R. NOYORI, *Org. Biomol. Chem.*, 2006, 4, (3), 393–406

A chiral bifunctional Ru catalyst (1) that was originally developed for asymmetric transfer hydrogenation of ketones and imines, has been applied to the enantioselective C–C bond formation reaction. The deprotonation of 1,3-dicarbonyl compounds with chiral amido Ru complexes leading to amine Ru complexes bearing C- or O-bonded enolates, followed by further reactions with electrophiles gives C-C bond formation products. (1) has the potential for stereoselective molecular transformation including enantioselective C–H, C–C as well as C–O and C–N bond formation.

FUEL CELLS

Single-Wall Carbon Nanotubes Supported Platinum Nanoparticles with Improved Electrocatalytic Activity for Oxygen Reduction Reaction

A. KONGKANAND, S. KUWABATA, G. GIRISHKUMAR and P. KAMAT, *Langmuir*, 2006, 22, (5), 2392–2396

Films of Pt/single wall C nanotubes (SWCNTs) cast on a rotating disk electrode exhibit a lower onset potential and a higher electron-transfer rate constant for O reduction, when compared to a Pt/C black catalyst. Improved stability of the SWCNT support is confirmed from the minimal change in the O reduction current during repeated cycling over 36 h. Pt/SWCNT may be used as DMFC and PEMFC cathodes.

Characterization of Electrode Structures and the Related Performance of Direct Methanol Fuel Cells

C. Y. CHEN and C. S. TSAO, *Int. J. Hydrogen Energy*, 2006, 31, (3), 391–398

An increase of ~ 25% in power performance was claimed to be achievable by controlling the pressure of the hot press in the MEA fabrication process for a given Pt loading. The improved performance of the MEA was attributed to the porosity of the cathode in which a network of macrofissures and sub-microfissures allows air to penetrate the cathode. The specific power density was found to almost double when the total porosity increased from 57% to 76%.

Electrocatalytic Activity of Ordered Intermetallic PtSb for Methanol Electro-Oxidation

L. ZHANG and D. XIA, *Appl. Surf. Sci.*, 2006, 252, (6), 2191–2195

Ordered intermetallic PtSb (1) was prepared by arc-melting followed by sintering. The electrooxidation of MeOH on (1) was investigated at room temperature by CV and chronoamperometry. (1) was catalytically more active than a polycrystalline Pt electrode surface according to the onset potential and current density.

Template Synthesis of Arrays of Nano Fuel Cells

K. W. LUX and K. J. RODRIGUEZ, *Nano Lett.*, 2006, 6, (2), 288–295

Pt-Cu nanowires were electrodeposited inside the cylindrical pores of an Anodisc filter membrane. The filter was then soaked in fuming HNO₃ to remove the Cu and construct an array of porous Pt electrodes (1). An array of nano fuel cells (2), each ~ 200 nm in diameter, was produced by utilising two arrays of (1) with a polymer electrolyte membrane or an electrolyte support matrix sandwiched between. (2) using aqueous NaBH₄ fuel gave power densities of ~ 1 mW cm⁻².

Methanol-Tolerant Oxygen Reduction Electrocatalysts Based on Pd-3D Transition Metal Alloys for Direct Methanol Fuel Cells

K. LEE, O. SAVADOGO, A. ISHIHARA, S. MITSUSHIMA, N. KAMIYA and K.-I. OTA, *J. Electrochem. Soc.*, 2006, 153, (1), A20–A24

Pd-based alloys (1), Pd-Co, -Ni and -Cr, have been developed as MeOH-tolerant O reduction electrocatalyst (2). (2) were fabricated by RF sputtering. The electrochemical characteristics of (2) for the ORR were determined in H₂SO₄ solution with and without MeOH at 30°C. (1) showed a higher ORR electrocatalytic activity than Pd, although lower than Pt. (1) also had no electrocatalytic activity for MeOH oxidation. The maximum electrocatalytic activities for ORR were observed for an alloy composition of ~ 60 at.% Pd in (1).

ELECTRICAL AND ELECTRONIC ENGINEERING

Oriented Self-Assembly of Cubic FePt Nanoparticles

N. SHUKLA, C. LIU and A. G. ROY, *Mater. Lett.*, 2006, 60, (8), 995–998

Attempts were made to synthesise single crystalline FePt nanoparticles (1) with cubic shapes. Particles with shapes that are close to cubic or rectangular were obtained. When deposited on surfaces these particles assemble with local order and a square lattice; they orient themselves with their [100] axes perpendicular to the surface and with local interparticle alignment of the [010] and [001] axes oriented parallel to the surface. These FePt nanocube films begin to overcome obstacles associated with magnetic data storage media based on self-oriented magnetic arrays of (1).

MEDICAL USES

The Chemistry of Dinuclear Analogues of the Anticancer Drug Cisplatin. A DFT/CDM Study

D. V. DEUBEL, *J. Am. Chem. Soc.*, 2006, 128, (5), 1654–1663

A combined DFT/CDM approach was used to study the formation mechanism of dinuclear Pt(II) μ -hydroxo complexes from cisplatin hydrolysis products, their interconversion, decomposition, and reactions with biomolecules. The results are reported to: (i) help assess if dinuclear metabolites play a role in cisplatin chemotherapy, and (ii) elucidate the toxicity and pharmacological inactivity of [*cis*-{Pt(NH₃)₂}(μ -OH)]₂²⁺.