

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Platinum-Catalyzed High Temperature Oxidation of Metals

Q. DONG, G. HULTQUIST, G. I. SPROULE and M. J. GRAHAM, *Corros. Sci.*, 2007, 49, (8), 3348–3360

Al, Cr, Ni and Zr were sputter-coated with porous Pt films (1). SIMS analysis on partly Pt-coated metal samples at different oxide depths in areas with Pt and in areas away from Pt indicated an enhanced inward oxide growth in the Pt area and at mm-ranged distance from the Pt area. Weight gain measurements on Pt-coated Ni samples showed a reduced or increased oxidation rate depending on the amount of (1).

SERS at Structured Palladium and Platinum Surfaces

M. E. ABDELSALAM, S. MAHAJAN, P. N. BARTLETT, J. J. BAUMBERG and A. E. RUSSELL, *J. Am. Chem. Soc.*, 2007, 129, (23), 7399–7406

Templated electrodeposition through colloidal templates was used to produce thin (< 1 μm) films (1) of Pt- and Pd-containing close packed hexagonal arrays of uniform sphere segment voids. The SERS spectra for benzenethiol adsorbed on the surfaces of (1) with different thicknesses and void diameters are reported. For 633 nm radiation, enhancement factors of 550 and 1800 can be obtained for Pt and Pd, respectively.

Martensitic Transformation in TiPd Shape Memory Alloys Studied by PAC Method with ¹⁸¹Ta Probes

A. KULINSKA and P. WODNIECKI, *Intermetallics*, 2007, 15, (9), 1190–1196

The perturbed angular correlation method was applied to study the martensitic phase transition of the title alloy doped with ¹⁸¹Hf/¹⁸¹Ta probe atoms. Strong dependences of the martensite start temperature (*M*_s) and the shape of the hysteresis loop (*T*_H) on the small admixture of the Hf impurities in TiPd compound were found. The observed decrease of the *M*_s value differs from the behaviour of TiNi, where adding Hf as the third element leads to a rise of *M*_s.

Deformation Tracks Distribution in Iridium Single Crystals Under Tension

P. PANFILOV, *J. Mater. Sci.*, 2007, 42, (19), 8230–8235

The deformation tracks distribution in a single crystal of f.c.c.-Ir (1), which exhibits cleavage after considerable elongation, is considered. Octahedral slip is the sole deformation mechanism in (1) at room temperature. In contrast to other f.c.c.-metals, the resource of plasticity of (1) is exhausted at the initial/early stages of plastic deformation, when the octahedral slip bands are homogeneously distributed on the working surface and necking is absent in the vicinity of the dangerous crack.

CHEMICAL COMPOUNDS

Self-Assembly of a Nanoscopic Platinum(II) Double Square Cage

S. GHOSH, S. R. BATTEN, D. R. TURNER and P. S. MUKHERJEE, *Organometallics*, 2007, 26, (13), 3252–3255

A rigid tripodal ligand (1) with an ester cap (1 = 1,1,1-tris(4-pyridyl)COOR, where R = PhCH(C₂H₅)) was designed and prepared. A 2:3 self-assembly of (1) with *cis*-(PEt₃)₂Pt(OTf)₂ as a 90° ditopic acceptor unit yielded an unusual 3D cage (2). Multinuclear NMR spectroscopy and single-crystal structure analysis were used to characterise (2).

Nickel(II), Palladium(II) and Platinum(II)

Complexes of *N*-Allyl-*N'*-pyrimidin-2-ylthiourea

S. S. KANDIL, S. M. A. KATIB and N. H. M. YARKANDI, *Transition Met. Chem.*, 2007, 32, (6), 791–798

The title complexes with *N*-allyl-*N'*-pyrimidin-2-ylthiourea (1) were synthesised in 1:1 and 1:2 [metal:ligand] stoichiometric ratios. The ¹H- and ¹³C- NMR chemical shifts revealed coordination of one pyrimidine-N and S atoms to Pt(II) and Pd(II). The IR spectra indicated (1) acts as a bidentate ligand towards Pt(II) and Pd(II), and coordinates *via* thione-S and a pyrimidine-N.

Synthesis and X-ray Structures of Water-Soluble Tris(hydroxymethyl)phosphine Complexes of Rhodium(I)

F. LORENZINI, B. O. PATRICK and B. R. JAMES, *Dalton Trans.*, 2007, (30), 3224–3226

H₂O-soluble Rh(I) complexes: RhCl(1,5-cod)(THP) (1), [Rh(1,5-cod)(THP)₂]Cl (2), RhCl(THP)₄ (3), and *trans*-RhCl(CO)(THP)₂ (4) (THP = P(CH₂OH)₃) have been synthesised and characterised. (1), (2) and (3) are reported to be the first potentially useful entries into Rh(I)-THP chemistry, while (1) and (4) are the first structurally characterised Rh(I)-THP complexes.

PHOTOCONVERSION

Highly Phosphorescent Perfect Green Emitting Iridium(III) Complex for Application in OLEDs

H. J. BOLINK, E. CORONADO, S. GARCIA SANTAMARIA, M. SESSOLO, N. EVANS, C. KLEIN, E. BARANOFF, K. KALYANASUNDARAM, M. GRAETZEL and MD. K. NAZEERUDDIN, *Chem. Commun.*, 2007, (31), 3276–3278

Bis-(2-phenylpyridine)(2-carboxy-4-dimethylamino-pyridine)iridium(III) (N984) was synthesised by reacting [Ir(ppy)₂(Cl)]₂ with methyl-dimethylamino-picolinate and Na₂CO₃ in 2-ethoxyethanol. A solution processable OLED device incorporating the yellow N984 complex displays electroluminescence spectra with a narrow bandwidth of 70 nm at half of its intensity, with colour coordinates that are very close to the PAL standard for a green emitter.

Periodic Mesoporous Silica having Covalently Attached Tris(bipyridine)ruthenium Complex: Synthesis, Photovoltaic and Electrochemiluminescent Properties

J. FONT, P. DE MARCH, F. BUSQUÉ, E. CASAS, M. BENITEZ, L. TERUEL and H. GARCÍA, *J. Mater. Chem.*, 2007, 17, (22), 2336–2343

A tris(bpy)Ru derivative with two terminal triethoxysilyl groups attached to one of the bpy ligands was used with TEOS for the preparation of a tris(bpy)Ru-containing mesoporous silica (1), using CTABr as a structure-directing agent. The tris(bpy)Ru at the walls in (1) gives its orange coloration. (1) exhibits photovoltaic ($V_{OC} = 140$ mV, $I_{SC} = 2.6$ μ A) and electrochemiluminescence activity ($\lambda_{max} = 610$ nm).

SURFACE COATINGS

Plasma-Enhanced Atomic Layer Deposition of Palladium on a Polymer Substrate

G. A. TEN EYCK, S. PIMANPANG, J. S. JUNEJA, H. BAKHRU, T. M. LU and G.-C. WANG, *Chem. Vap. Deposition*, 2007, 13, (6–7), 307–311

Pd has been deposited on air-exposed, annealed poly(*p*-xylylene) (PPX) at 80°C using a remote, inductively coupled, H₂/N₂ plasma with Pd(hfac)₂ as the precursor. By optimising the mixture of H₂ and N₂, the PPX surface is modified to introduce active sites allowing the chemisorption of the Pd(hfac)₂. In addition, enough free H atoms are available at the surface for ligand removal and Pd reduction, while at the same time, enough H atoms are consumed in the plasma to ensure there is no degradation of the PPX.

APPARATUS AND TECHNIQUE

Classification of Multiple Defect Concentrations in White Wine by Platinum Microelectrode Voltammetry

L. FRANCIOSO, R. BJORKLUND, T. KRANTZ-RÜLCKER and P. SICILIANO, *Sens. Actuators B: Chem.*, 2007, 125, (2), 462–467

Concentrations of defect pairs added to a white wine were classified by voltammetric measurements on interdigitated Pt microelectrodes using principal component analysis of the current responses. Ascorbic acid/acetaldehyde, ascorbic acid/SO₂ and acetaldehyde/SO₂ combinations of 0, 1, 2 and 3 mM concentrations were investigated.

Amperometric Glucose Biosensor Based on Electrodeposition of Platinum Nanoparticles onto Covalently Immobilized Carbon Nanotube Electrode

X. CHU, D. DUAN, G. SHEN and R. YU, *Talanta*, 2007, 71, (5), 2040–2047

A fabricated GOx/Au_{nano}/Pt_{nano}/CNT electrode (1) was covered with a thin layer of Nafion to avoid the loss of GOx (glucose oxidase) and to improve the anti-interferent ability. (1) exhibited rapid response for glucose in the absence of a mediator. The biosensor based on (1) had good reproducibility and stability for the determination of glucose.

Preparation and Characterisation of Palladium-Loaded Polypropylene Porous Hollow Fibre Membranes for Hydrogenation of Dissolved Oxygen in Water

R. VAN DER VAART, V. I. LEBEDEVA, I. V. PETROVA, L. M. PLYASOVA, N. A. RUDINA, D. I. KOCHUBEY, G. F. TERESHCHENKO, V. V. VOLKOV and J. VAN ERKEL, *J. Membrane Sci.*, 2007, 299, (1–2), 38–44

Pd could be deposited on a hydrophobic porous Accurel polypropylene membrane hollow fibre, while keeping its hydrophobic nature. Pd loadings as low as 0.36% (w/w) were sufficient to catalyse the hydrogenation of dissolved O₂ while maintaining diffusion limited kinetics. A fast O₂ removal system was obtained that has the potential of maintaining removal rate, even at very low concentrations of O₂.

HETEROGENEOUS CATALYSIS

Effect of Palladium on Sulfur Resistance in Pt–Pd Bimetallic Catalysts

H. JIANG, H. YANG, R. HAWKINS and Z. RING, *Catal. Today*, 2007, 125, (3–4), 282–290

The interactions of H₂ and H₂S with Pt–Pd bimetallic catalysts (1) were studied using DFT. When alloying the Pt catalyst with a small amount of Pd at a particular surface atomic ratio range, the adsorptions of both H₂ and H₂S were enhanced, but the adsorption energy of H₂ increased more than that of H₂S. The desorption energy of H₂ from Pt or Pd, as well as of (1) supported on a zeolite, were calculated by TPD; these values were compared against the DFT results to explain why (1) has better S resistance than Pt.

The Effect of Ionic Liquid in Supported Ionic Liquid Catalysts (SILCA) in the Hydrogenation of α,β -Unsaturated Aldehydes

P. VIRTANEN, H. KARHU, K. KORDAS and J.-P. MIKKOLA, *Chem. Eng. Sci.*, 2007, 62, (14), 3660–3671

Pd nanoparticles/ionic liquid layer/active C cloth SILCAs (1) were successfully employed in two different hydrogenation processes. Leaching of both Pd and ionic liquids was found to be negligible, and not the reason for slow deactivation of (1). The ionic liquid layer residing on the support of (1) can either enhance the reaction rate or affect the selectivity profile of the reaction.

Palladium Ethylthioglycolate Modified Silica–A New Heterogeneous Catalyst for Suzuki and Heck Cross-Coupling Reactions

M. AL-HASHIMI, A. C. SULLIVAN and J. R. H. WILSON, *J. Mol. Catal. A: Chem.*, 2007, 273, (1–2), 298–302

A silica-supported S-containing ethylthioglycolate material that readily binds Pd from solutions of Pd(OAc)₂ was synthesised. This affords an active and recyclable solid phase catalyst (1). Close to quantitative conversions were observed with (1) for Suzuki reactions in less than 2 h. The Heck reactions were complete within 24 h.

Effect of Liquid Property on Adsorption and Catalytic Reduction of Nitrate over Hydrotalcite-Supported Pd-Cu Catalyst

Y. WANG, J. QU and H. LIU, *J. Mol. Catal. A: Chem.*, 2007, 272, (1–2), 31–37

Nitrate ions were adsorbed by Pd-Cu/hydrotalcite (1) at 10, 25 and 35°C. Higher reaction temperature accelerated nitrate adsorption and reduction, and simultaneously decreased the accumulation of NO_2^- and NH_4^+ . pH and coexisted ions in the H_2O also showed influence on nitrate removal. The activity of (1) was maintained after repeated use.

Combining Diffuse Reflectance Infrared Spectroscopy (DRIFTS), Dispersive EXAFS, and Mass Spectrometry with High Time Resolution: Potential, Limitations, and Application to the Study of NO Interaction with Supported Rh Catalysts

M. A. NEWTON, A. J. DENT, S. G. FIDDY, B. JYOTI and J. EVANS, *Catal. Today*, 2007, 126, (1–2), 64–72

The title experiment was used to study the oxidation (by NO) and reduction (by H_2) of Rh/ $\gamma\text{-Al}_2\text{O}_3$. The specific role that the linear NO^+ species has in both oxidation and reduction of Rh, and the role it may play reactively at elevated temperatures were determined. New information was gained about the physical character of the linear NO^+ species and the nature of the Rh phase/sites with which it is associated.

HOMOGENEOUS CATALYSIS

Phosphine Oxides as Stabilizing Ligands for the Palladium-Catalyzed Cross-Coupling of Potassium Aryldimethylsilanolates

S. E. DENMARK, R. C. SMITH and S. A. TYMONKO, *Tetrahedron*, 2007, 63, (26), 5730–5738

The Pd-catalysed cross-coupling reaction of potassium (4-methoxyphenyl)dimethylsilanolate with aryl bromides has been achieved using $\text{Ph}_3\text{P}(\text{O})$ as a stabilising ligand. Allylpalladium(II) chloride dimer was employed as a precatalyst. Unsymmetrical biaryls were prepared from a variety of aryl bromides in good yield with short reaction times.

Catalysts Based on Palladium Dendrimers

R. ANDRÉS, E. DE JESÚS and J. C. FLORES, *New J. Chem.*, 2007, 31, (7), 1161–1191

The advances in Pd-catalysed reactions using dendrimer-based catalysts are reviewed. This includes the role of Pd dendrimers as: (a) soluble macromolecules for the support of catalysts, that are separable by nanofiltration techniques; (b) ligand-modifiers that can tune the solubility of the catalyst; (c) spacers for catalyst immobilisation on silica or polymers; and (d) precursors for the synthesis of mono- and bimetallic nanoparticles of controlled size and narrow size distribution. Examples of catalysis with related metal systems, such as star-shaped molecules or hyperbranched polymers, are also included. (169 Refs.)

Pd-Smopex-111: A New Catalyst for Heck and Suzuki Cross-Coupling Reactions

X. JIANG, J. SCLAFANI, K. PRASAD, O. REPIC and T. J. BLACKLOCK, *Org. Process Res. Dev.*, 2007, 11, (4), 769–772

Pd was loaded onto Smopex-111 by stirring a pre-filtered toluene solution of $\text{Pd}(\text{OAc})_2$ and Smopex-111 heated to 70°C. After filtration and washing, the complex was dried to give Pd-Smopex-111 (1) with a Pd loading of 4.4–4.7 wt.%. (1) was a highly active catalyst for Heck and Suzuki cross-coupling reactions. Both electron-donating and electron-withdrawing groups on the aryl bromide were tolerated. (1) is recyclable with no noticeable change in activity. Isolation of (1) involves simple filtration.

A Convenient Catalyst System for Microwave Accelerated Cross-Coupling of a Range of Aryl Boronic Acids with Aryl Chlorides

M. L. CLARKE, M. B. FRANCE, J. A. FUENTES, E. J. MILTON and G. J. ROFF, *Beilstein J. Org. Chem.*, 2007, 3, 18

A readily prepared, air-stable Pd precatalyst derived from the amine-phosphine ligand, dcpmp, promoted Suzuki cross-coupling between activated aryl chlorides and a range of boronic acids under microwave heating conditions. High yields of the product biaryls were obtained in 15 min or less. Heavily fluorinated boronic acids do not participate in these Suzuki couplings due to protodeboronation.

Catalytic Hydrogenation of Nitrile Rubber Using Palladium and Ruthenium Complexes

G. A. S. SCHULZ, E. COMIN and R. F. DE SOUZA, *J. Appl. Polym. Sci.*, 2007, 106, (1), 659–663

The hydrogenation of acrylonitrile-butadiene copolymer (NBR) using $\text{Pd}(\text{OAc})_2$ or $\text{RuCl}_2(\text{PPh}_3)_3$ catalysts has been investigated in order to produce a totally saturated nitrile rubber. The hydrogenation of NBR is effective with both catalysts and under the appropriate conditions total conversion to HNBR is achievable. $\text{Pd}(\text{OAc})_2$ requires harsher reaction conditions and has the drawback of gel formation under high conversion. The degree of hydrogenation was determined by IR and NMR spectroscopy.

Hydroformylation of Higher Olefin in Halogen-Free Ionic Liquids Catalyzed by Water-Soluble Rhodium-Phosphine Complexes

Q. LIN, W. JIANG, H. FU, H. CHEN and X. LI, *Appl. Catal. A: Gen.*, 2007, 328, (1), 83–87

The biphasic hydroformylation of higher olefins was carried out in 1-*n*-alkyl-3-methylimidazolium *p*-toluenesulfonate using Rh-TPPTS complexes as the catalyst. High activity and chemoselectivity for aldehyde with retention of the catalyst in the ionic liquid phase was exhibited. The ionic liquid containing catalyst can be easily separated and reused. The reaction rate is dependent on the cation and anion of the ionic liquids used. Furthermore, the reaction rate was accelerated when the chain length of the alkyl in the ionic liquids was comparable with that of the olefin.

FUEL CELLS

Combinatorial Electrochemical Cell Array for High Throughput Screening of Micro-Fuel-Cells and Metal/Air Batteries

R. JIANG, *Rev. Sci. Instrum.*, 2007, 78, (7), 072209

An electrochemical cell array (1) was designed that contains a common air electrode and 16 microanodes for high-throughput screening of both fuel cells (based on PEM) and metal/air batteries. Electrode materials were coated on the anodes of the electrochemical cell array and screened by switching a graphite probe from one cell to the others. (1) was used to study DMFCs, including high-throughput screening of electrode catalysts involving Pt and Ru, and determination of optimum operating conditions.

Catalysts for Direct Ethanol Fuel Cells

E. ANTOLINI, *J. Power Sources*, 2007, 170, (1), 1–12

The electrocatalysts which have been tested as anode and cathode materials for DEFCs are reviewed, with attention focused on the catalyst composition, degree of alloying, presence of oxides and activity for the EtOH oxidation reaction. Conversely to the MeOH oxidation reaction, the best binary catalyst for EtOH oxidation in acid environment is not Pt-Ru but Pt-Sn. Ternary Pt-Ru- and Pt-Sn-based electrocatalysts are also described. Pt-Pd (9:1) showed higher EtOH tolerance than Pt when used as cathode material. (90 Refs.)

Carbon Nanotubes Supported Pt-Ru-Ni as Methanol Electro-Oxidation Catalyst for Direct Methanol Fuel Cells

F. YE, S. CHEN, X. DONG and W. LIN, *J. Nat. Gas Chem.*, 2007, 16, (2), 162–166

Pt-Ru/CNTs and Pt-Ru-Ni/CNTs catalysts were prepared by reduction of metal precursors with NaBH₄ at room temperature. The particle size of the Pt-Ru-Ni/CNTs catalyst is ~ 4.8 nm. The catalytic activity and stability for MeOH electrooxidation were measured by electrochemical impedance spectroscopy, linear sweep voltammetries, and chronoamperometry. The catalytic activity and stability of the Pt-Ru-Ni/CNTs catalyst are higher than those of the Pt-Ru/CNTs catalyst.

Pt and Ni Carbon Nitride Electrocatalysts for the Oxygen Reduction Reaction

V. DI NOTO, E. NEGRO, R. GLIUBIZZI, S. GROSS, C. MACCATO and G. PACE, *J. Electrochem. Soc.*, 2007, 154, (8), B745–B756

A precursor (1) was prepared from a Pt chloride and a Ni cyanometallate complex in the presence of sucrose, which acts as an organic binder. The thermal decomposition of (1), which was studied at 400–700°C, and the procedure for activating the products, were critical. The electrochemical efficiency in the O reduction reaction of the title electrocatalysts proved to be much higher than that of standard materials having a similar Pt content.

MEDICAL USES

Two Different Types of Age-Hardening Behaviors in Commercial Dental Gold Alloys

K. HISATSUNE, T. SHIRAIISHI, Y. TAKUMA, Y. TANAKA and R. H. LUCIANO, *J. Mater. Sci.: Mater. Med.*, 2007, 18, (4), 577–581

Age-hardening behaviour during continuous heating in the title alloys was studied by means of electrical resistivity measurements, hardness tests and XRD. Two distinguishable behaviours were found. The difference was attributed to the amount of Pt, and the atomic ratio of Au and Cu in each alloy. The phase transformations during continuous heating progressed in two stages. Increase of the Pt addition in the alloys retards the rate of the reaction and decreases the amount of the first stage.

Hardening and Overaging Mechanism of a Commercial Au–Ag–Cu–Pd Dental Alloy

H.-I. KIM, G.-H. JEON, S.-J. YI, Y. H. KWON and H.-J. SEOL, *J. Alloys Compd.*, 2007, 441, (1–2), 124–130

The ageing behaviour and age-hardening of the title alloy (1) with small amounts of Pt, Zn and Ir (48.0 wt.% Au–32.5 wt.% Ag–8.0 wt.% Cu–7.4 wt.% Pd–2.0 wt.% Pt–2.0 wt.% Zn–0.1 wt.% Ir) was investigated. (1) showed apparent age-hardenability at the ageing temperature of 400°C. By ageing, the hardness of the solution-treated specimen began to increase and reached a maximum value, and then the hardness decreased continuously by further ageing.

Guanine Binding to Dirhodium Tetracarboxylate Anticancer Complexes: Quantum Chemical Calculations Unravel an Elusive Mechanism

D. V. DEUBEL and H. T. CHIFOTIDES, *Chem. Commun.*, 2007, (33), 3438–3440

The mechanism of guanine binding to dirhodium tetracarboxylates, representing an emerging class of metal–metal-bonded antitumour complexes, has been established. Numerous experiments led to the characterisation of the reactants and products, but the reaction mechanism had not been established. High-level quantum chemical calculations suggest a multiple-step mechanism *via* an axial Gua-N7 adduct and an ax–eq carboxylate chelate as unexpected key intermediates.

Synthesis, Characterization and Antimalarial Activity of New Iridium–Chloroquine Complexes

M. NAVARRO, S. PEKERAR and H. A. PÉREZ, *Polyhedron*, 2007, 26, (12), 2420–2424

Chloroquine base (CQ) reacted with [Ir(COD)Cl]₂ and IrCl₃·3H₂O to give Ir(CQ)Cl(COD) (1) and Ir₂Cl₆(CQ)·3H₂O (2), respectively. Reaction of [Ir(COD)Cl]₂ with CQ in the presence of NH₄PF₆ gave [Ir(CQ)(Solv)₂]PF₆ (3). Complexes (1)–(3) were evaluated *in vitro* against *Plasmodium falciparum*. Comparison of the IC₅₀ values obtained with complexes (1)–(3) with that for chloroquine diphosphate indicated a higher activity for (2), while (1) and (3) showed a similar and lower activity, respectively.