

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Synthesis and Characterization of a New Modification of PtAl

C. WEIDENTHALER, W. BRIJOUX, T. OULD-ELY, B. SPLIETHOFF and H. BÖNNEMANN, *Appl. Organomet. Chem.*, 2003, 17, (9), 701–705

A new PtAl phase (1), which is stable at room temperature under oxidising conditions, was synthesised at 200°C and 5 MPa. *In situ* high-temperature XRD experiments in air were performed to study the thermal behaviour of (1). At 400–700°C, Pt₃Al₃ formed as an intermediate phase. At higher temperature the Pt₃Al₃ decomposes into Pt and Al₂O₃.

Oxidation of FePt Nanoparticles

C. LIU, T. J. KLEMMER, N. SHUKLA, X. WU, D. WELLER, M. TANASE and D. LAUGHLIN, *J. Magn. Magn. Mater.*, 2003, 266, (1–2), 96–101

Monodispersed FePt nanoparticles were synthesised using the airless operation technique based on the decomposition of Fe(CO)₅ and reduction of Pt acetylacetonate. The particle solution was then washed and subsequently deposited onto a thermally oxidised Si substrate. Nanoparticle assemblies were formed after solvent evaporation. The samples were heat-treated using rapid thermal annealing at 650°C for 30 min, in Ar with < 1 ppm of O₂. Oxidation has to be avoided to obtain the FePt L1₀ phase. If O₂ is present, phases such as FePt₃, Fe₃O₄ and Pt form.

Ferromagnetism of FePt₃ Films Induced by Ion-Beam Irradiation

S. MAAT, A. J. KELLOCK, D. WELLER, J. E. E. BAGLIN and E. E. FULLERTON, *J. Magn. Magn. Mater.*, 2003, 265, (1), 1–6

Both epitaxial and polycrystalline FePt₃ films were grown in the chemically ordered L1₂ phase and were non-magnetic at room temperature. Upon irradiation with 700 keV N⁺ ions at a dose of 1 × 10¹⁶ ions cm⁻² the chemical order was destroyed and ferromagnetism was induced.

Analysis of Surface and Bulk Behavior in Ni–Pd Alloys

G. BOZZOLO and R. D. NOEBE, *Acta Mater.*, 2003, 51, (15), 4395–4409

The Bozzolo–Ferrante–Smith method was used to study Ni–Pd alloy surfaces. Large-scale atomistic simulations were performed to investigate surface segregation profiles as a function of temperature, crystal face and composition. Pd enrichment of the first layer was observed in (1 1 1) and (1 0 0) surfaces, and enrichment of the top two layers occurred for (1 1 0) surfaces. In all cases, the segregation profile showed alternate planes enriched and depleted in Pd. A weak ordering tendency was observed at low temperatures.

CHEMICAL COMPOUNDS

Unexpected Effect of Cyclodextrins on Water-Soluble Rhodium Complexes

L. CARON, M. CANIPELLE, S. TILLOY, H. BRICOUT and E. MONFLIER, *Eur. J. Inorg. Chem.*, 2003, (4), 595–599

[HRh(CO){(*p*-*t*BuC₆H₄)P(*m*-C₆H₄SO₃Na)₂}₃] can be partially converted in the presence of β-cyclodextrin or randomly methylated β-cyclodextrin into the HO complex [HORh(CO){(*p*-*t*BuC₆H₄)P(*m*-C₆H₄SO₃Na)₂}₂], under N₂, or to the hydrido complex [HRh(CO)₂{(*p*-*t*BuC₆H₄)P(*m*-C₆H₄SO₃Na)₂}₂], under CO. No such effect was shown by [HRh(CO){P(*m*-C₆H₄SO₃Na)₃}₃].

ELECTROCHEMISTRY

Kinetics and Mechanism of the Oxidation of Sodium Dithionite at a Platinum Electrode in Alkaline Solution

E. GASANA, P. WESTBROEK, K. DE WAELE, E. TEMMERMAN, K. DE CLERCK and P. KIEKENS, *J. Electroanal. Chem.*, 2003, 553, 35–42

The oxidation of Na dithionite (1) in alkaline solution was studied by CV at a stationary and rotating Pt disc electrode. The reaction proceeds in two steps, with sulfite as a relatively stable intermediate and sulfate as a final product. The kinetics of the oxidation wave show a reaction order of 0.5 with respect to (1).

PHOTOCONVERSION

Imaging of Catalytic Activity of Platinum on p-InP for Photocathodical Hydrogen Evolution

A. BARKSCHAT, H. TRIBUTSCH and J. K. DOHRMANN, *Sol. Energy Mater. Sol. Cells*, 2003, 80, (4), 391–403

Pt was deposited photocathodically on single-crystalline *p*-InP from aqueous H₂PtCl₆. Subsequent spatially resolved photocurrent measurements in H₂SO₄ at different potentials and comparison with optical micrographs of the Pt deposits showed that the catalytically most active deposits were formed at low light intensity (45 mW cm⁻²) and relatively negative potentials (−0.3 vs. SCE).

Orientation-Dependent Phosphorescence from Nanocrystals of Platinum Tetraphenylporphyrin Grown on Alkali Halides

H. YANAGI and T. SHIBUTANI, *Thin Solid Films*, 2003, 438–439, 33–38

Epitaxially oriented nanocrystals of PtTPP (1) were grown by vapour deposition on a cleaved surface of K halide single crystals. (1), deposited on the KCl (0 0 1) surface kept at 200°C, formed pyramidal crystals showing red phosphorescence. However, (1) deposited on the KBr (0 0 1) surface kept at 200°C formed plate-like crystals (2). The monoclinic molecular packing in (2) gave phosphorescence quenching.

ELECTRODEPOSITION AND SURFACE COATINGS

Investigation of the Interfacial Structure of Ultra-Thin Platinum Film Deposited by Cathodic-Arc

P. D. SWIFT, D. M. SOLINA, R. W. CHEARY and G. M. MCCREDIE, *Thin Solid Films*, 2003, 440, (1–2), 117–122

Ultrathin films of Pt (1) (15–65 Å) were deposited on Si substrates, using cathodic-arc deposition (2). The structure of the deposited (1) was found to consist of 3 layers: the Pt film, a Si oxide layer and a Pt silicide layer. In contrast to DC magnetron and electron beam deposited films, the silicide layer of (1) has a higher density and greater thickness. This is attributed to the higher energy of this deposition process. The attributes of (1) suggest that (2) is only suitable for producing mirrors of materials that do not react with each other, such as Pt and SiO₂.

Synthesis and Characterization of Fe_{100-x}Pt_x Alloy Thin Films

T. MAHALINGAM, J. P. CHU, J. H. CHEN, C. L. CHIANG and S. F. WANG, *Mater. Chem. Phys.*, 2003, 82, (2), 335–340

The title films (1) with various Pt compositions ($x = 15, 24, 46$ and 78 at.%) were synthesised by magnetron sputtering. The XRD patterns of as-deposited (1) with all compositions exhibited a disordered phase with f.c.c. structure. Annealing of Fe₈₄Pt₁₆ films at high temperatures yielded an ordered L1₀ γ₂ phase with f.c.t. structure. DSC studies revealed exothermic peaks for phase transformation in different alloy compositions. The activation energies for phase transformations of (1) were found to increase with Pt concentration.

Enhanced Hydrogen Sorption Capacities and Kinetics of Mg₂Ni Alloys by Ball-Milling with Carbon and Pd Coating

R. JANOT, L. AYMARD, A. ROUGIER, G. A. NAZRI and J. M. TARASCON, *J. Mater. Res.*, 2003, 18, (8), 1749–1752

Mg₂Ni–C composites (1) were prepared by ball-milling the Mg₂Ni alloy in the presence of preground graphite and Pd-coated Mg₂Ni alloy powders were obtained by controlled chemical deposition of Pd on the alloy surface. Optimised pregrinding of C enhances the H₂ desorption capacity of (1) to 2.6 wt.% at 150°C. Pd deposition raises it further to 2.8 wt.%.

Electrochemical Synthesis of Zeolite-Like Ruthenium-Based Hexacyanometalates Multi-Film Assemblies

K. KASEM, F. R. STELDT, T. J. MILLER and A. N. ZIMMERMAN, *Microporous Mesoporous Mater.*, 2003, 66, (1), 133–141

CV was used to synthesise zeolite-like films of K_x⁺Ru_y[Fe(CN)₆]_z (RF) or Ru hexacyanoferrate and K_x⁺Ru_y[Ru(CN)₆]_z (RR) or Ru hexacyanoruthenate. Formation of porous multi-film assemblies of Prussian blue (PB) over RF was achieved by either direct electrodeposition of PB over RF or RF over PB during repetitive potential cycling, or by electrochemically driven insertion–substitution methods.

HETEROGENEOUS CATALYSIS

Ethylene Production Using a Pd and

Ag–Pd–Y-Zeolite Catalyst in a DC Plasma Reactor

C. L. GORDON, L. L. LOBBAN and R. G. MALLINSON, *Catal. Today*, 2003, 84, (1–2), 51–57

The addition of Pd to a NaOH-treated zeolite in a DC plasma reactor, using a feed of CH₄, H₂ and O₂ (< 2.5%), gives the same CH₄ conversion of 20–60% as the reactor without the Pd. However the initial acetylene produced is selectively hydrogenated *in situ* to ethylene. The catalyst is most selective ~ 45°C, where it produces ethylene:ethane of ~ 4–1 with no acetylene. Further increases in selectivity and operating temperature were achieved by adding Ag. The system has achieved ethylene yields as high as 30%, with H₂ yields of 40% and little production of the combustion products CO₂ and H₂O.

Solvent-Free Pd-Catalysed N-Arylation of Amines, Amides and Diaza-18-Crown-6

G. A. ARTAMKINA, M. V. ERMOLINA and I. P. BELETSKAYA, *Mendeleev Commun.*, 2003, (4), 158–160

The N-arylation of amines, amides and diaza-18-crown-6 with weakly activated aryl bromides catalysed by Pd⁰/L, and the arylation of 2-pyrrolidone with 2-bromothiophene catalysed by CuI/1,2-di(methylamino)cyclohexane were performed without solvent at 60–100°C. The addition of graphite prevents caking of the reaction mixture. The arylation products were obtained in good yields (60–78%).

Synthesis and Characterization of Palladium

Containing Membranes Based upon Polyacrylic Acid

A. BEYER, R. SCHOMÄCKER and K.-H. REICHERT, *Colloid Polym. Sci.*, 2003, 281, (9), 862–868

Porous catalytic membranes were prepared by crosslinking polyacrylic acid dispersions with a bifunctional crosslinker in the presence of Pd particles. Pd nanoparticles, stabilised with polystyrene-block-polyethyleneoxide, were immobilised in the polymer network in different ways. The polymer/Pd network was prepared as thin flat membranes and dried, retaining the porosity and 3D network structure. Different reduction and preparation methods were used to obtain differences in particle size and distribution of the Pd.

Ir/SiO₂ as a Highly Active Catalyst for the Selective Reduction of NO with CO in the Presence of O₂ and SO₂

M. HANEDA, T. YOSHINARI, K. SATO, Y. KINTAICHI and H. HAMADA, *Chem. Commun.*, 2003, (22), 2814–2815

SiO₂-supported Pt, Rh, Pd and Ir catalysts were prepared by impregnating SiO₂ with aqueous solutions of their salts. Ir/Al₂O₃ was also prepared. Ir/SiO₂ gave excellent activity with respect to NO reduction with CO in the presence of O₂ and SO₂. This could be due to the formation of a *cis*-type coordinated species of NO and CO to one Ir atom, a possible reaction intermediate in the formation of N₂.

The Os/Cu–Al-Hydrotalcite Catalysed Hydroxylation of Alkenes

H. B. FRIEDRICH, M. GOVENDER, X. MAKHOBA, T. D. NGCOBO and M. O. ONANI, *Chem. Commun.*, 2003, (23), 2922–2923

Os/Cu–Al-hydrotalcite (1) was prepared by precipitation with *N*-methylmorpholine oxide as cooxidant. (1) heterogeneously catalyses the hydroxylation of olefins to give diols selectively and in high yield. Heat-treating (1) initially has a beneficial effect, with 200°C being the optimal temperature. (1) calcined at 200°C reacted faster than uncalcined (1). Os does not leach into the reaction solution.

Scope, Kinetics, and Mechanistic Aspects of Aerobic Oxidations Catalyzed by Ruthenium Supported on Alumina

K. YAMAGUCHI and N. MIZUNO, *Chem. Eur. J.*, 2003, 9, (18), 4353–4361

Ru/Al₂O₃ (1) was obtained by modification of the preparation of Ru(OH)₃·*n*H₂O. (1) showed high activity for the oxidation of activated, nonactivated, and heterocyclic alcohols, diols, and amines at 1 atm of O₂. (1) could be reused seven times without a loss of catalytic activity and selectivity for the oxidation of benzyl alcohol. The oxidation proceeds through an alcoholate/β-hydride elimination mechanism. The β-hydride elimination is a rate-limiting step.

HOMOGENEOUS CATALYSIS

Additive Effects in Palladium–Indium Mediated Barbier Type Allylations

L. A. T. CLEGHORN, I. R. COOPER, R. GRIGG, W. S. MacLACHLAN and V. SRIDHARAN, *Tetrahedron Lett.*, 2003, 44, (43), 7969–7973

The effect of adding various amines (1 equiv.) or CuI (0.2 equiv.) to a Pd/In bimetallic cascade reaction was examined. In the class 1 cascade reaction of aldehydes, aryl iodides and allene, generating homoallylic alcohols, the reaction time was reduced from 16 to 2 h. This was accompanied by an impressive increase in yield. The amine additives aid the solvation of the In powder (accelerating the rate of transmetalation) and protect the catalytically active Pd species. All the cyclic amines improved yield.

Assignment of the Structure of a Ru(II)–BINAP Catalyst

L. DIMICHELE, S. A. KING and A. W. DOUGLAS, *Tetrahedron: Asymmetry*, 2003, 14, (22), 3427–3429

A Ru(II)–BINAP catalyst (1) was prepared from cyclooctadienyl Ru dichloride and (R)–BINAP in the presence of triethylamine. The reaction was carried out in toluene at reflux. The structure of (1) was identified using NMR spectroscopy as the diethylammonium salt $[(C_2H_5)_2NH_2]^+ [Ru_2Cl_5((R)-BINAP)_2]^-$. Due to the saturated octahedral environment of (1), activation of (1) with acid is necessary to allow low pressure (40 psi) and low temperature (40°C) catalytic hydrogenation reactions.

FUEL CELLS

Composite Electrodes Made of Pt Nanoparticles Deposited on Carbon Nanotubes Grown on Fuel Cell Backings

X. SUN, R. LI, D. VILLERS, J. P. DODELET and S. DÉSILETS, *Chem. Phys. Lett.*, 2003, 379, (1–2), 99–104

Multiwalled C nanotubes (MWCNTs), with typical lengths of 20 μm and diameters of 40 nm, were grown directly on C paper backing. A sulfonic acid–silicate intermediate was used to deposit Pt nanoparticles on the MWCNTs in order to obtain an electrode for electrocatalysis. CV showed that there is electrical contact through the MWCNTs between the Pt particles and the C paper backing.

Electro-Oxidation of Methanol and Ethanol on Poly(3,4-Ethylenedioxythiophene) with Dispersed Pt, Pt + Sn, and Pt + Pb Particles

S. BIALLOZOR, A. KUPNIEWSKA and V. JASULAITENE, *Fuel Cells*, 2003, 3, (1–2), 8–14

Sn and Pb additives were found to increase the catalytic activity of Pt particles dispersed on a PEDT layer deposited on Au or steel towards anodic oxidation of MeOH and EtOH. In the presence of Sn, the steady-state current density of MeOH oxidation increases ~ × 100, while Pb only promotes the Pt catalyst activity by ~ × 2. The Sn promotion effect may be due to a homogeneous catalytic reaction with the Sn(IV) and Sn(II) ions participating as mediators.

Modeling the Electro-Oxidation of CO and H₂/CO on Pt, Ru, PtRu and Pt₃Sn

P. LIU, A. LOGADOTTIR and J. K. NØRSKOV, *Electrochim. Acta*, 2003, 48, (25–26), 3731–3742

DFT calculations were used to describe the adsorption of H₂, CO and H₂O on the close packed surfaces of Pt, Ru, PtRu and Pt₃Sn. The calculated adsorption energetics were used in a model to describe the electrooxidation of CO and H₂ at conditions relevant to a PEMFC anode. The model showed that Ru, PtRu and Pt₃Sn begin to oxidise CO at lower potentials than Pt. PtRu was shown to have considerably lower overpotential for H₂ oxidation in the presence of CO than Pt. Pt₃Sn was even better than PtRu, while Ru was considerably poorer than Pt.

Development of Residential PEFC Cogeneration Systems: Ru Catalyst for CO Preferential Oxidation in Reformed Gas

M. ECHIGO, N. SHINKE, S. TAKAMI, S. HIGASHIGUCHI, K. HIRAI and T. TABATA, *Catal. Today*, 2003, 84, (3–4), 209–215

A novel Ru/Al₂O₃ catalyst (1) was prepared by an impregnation method. The performance of (1) in a single-stage CO preferential oxidation removal reactor (2) was investigated for residential PEFC cogeneration systems. The outlet CO concentration of (2) was reduced to < 1 ppm even at [O₂]/[CO] = 1.5. A natural gas fuel processor equipped with (2) achieved the target thermal efficiency of 77% (LHV).