

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Size Effects on the Thermal Conductivity of Polycrystalline Platinum Nanofilms

Q. G. ZHANG, B. Y. CAO, X. ZHANG, M. FUJII and K. TAKAHASHI, *J. Phys.: Condens. Matter*, 2006, 18, (34), 7937–7950

The thicknesses of the studied polycrystalline Pt nanofilms (1) ranged from 15.0–63.0 nm and the mean grain sizes varied from 9.5–26.4 nm. The thermal conductivities of (1) measured by a direct electrical heating method are greatly reduced from the bulk values, due mainly to grain-boundary scattering.

Demixing of Solid-Soluted Co-Pd Binary Alloy Induced by Microwave Plasma Hydrogen Irradiation Technique

T. TOKUNAGA, Y. HAYASHI, T. FUJITA, S. R. P. SILVA and G. A. J. AMARATUNGA, *Jpn. J. Appl. Phys., Part 2*, 2006, 45, (32), L860–L863

Demixing in a solid-soluted Co-40 at.% Pd alloy was induced by microwave plasma H irradiation on a mixture of Pd-Co island grains on a Si substrate. Microstructure observation and X-ray microanalysis by TEM before and after the irradiation provided evidence of demixing in the metallic Co-Pd alloys. The possibility of the decomposition into Pd hydride and Co under irradiation at high temperatures is indicated.

Surface Segregation and Homogenization of Pd₇₀Ag₃₀ Alloy Nanoparticles

K.-W. WANG, S.-R. CHUNG and T.-P. PERNG, *J. Alloys Compd.*, 2006, 422, (1–2), 223–226

In this study Pd₇₀Ag₃₀ nanoparticles (1) with the smallest size and the highest homogeneity were prepared using the strong reducing agent NaBH₄. After heating (1), the surface segregation of Ag was small and the sintering was retarded by the high surface Pd concentration or by the residual B. There was significant surface segregation of Ag and sintering for (1) prepared by HCHO, where a higher concentration gradient existed inside (1). The behaviour of (1) prepared by N₂H₄ was intermediate between those of the other two samples.

Crystal Growth, Structure, Magnetic, and Transport Properties of TbRhIn₅

W. M. WILLIAMS, L. PHAM, S. MAQUILON, M. MOLDOVAN, Z. FISK, D. P. YOUNG and J. Y. CHAN, *Inorg. Chem.*, 2006, 45, (12), 4637–4641

Single crystals of TbRhIn₅ (1) were synthesised using the flux growth method. (1) is isostructural to CeRhIn₅. The easy axis of magnetisation in (1) ($T_N = 47$ K) is along the *c* axis. T_N is enhanced by ~ 24% compared to that in TbIn₃ ($T_N = 36$ K). Although (1) is not a heavy fermion superconductor, it does have strong antiferromagnetic correlations.

CHEMICAL COMPOUNDS

Growth and Characterization of Partially Oxidized Platinum Polymers in Nanoscale Templates

B. M. ANDERSON, S. K. HURST, L. SPANGLER, E. H. ABBOTT, P. MARTELLARO, P. J. PINHERO and E. S. PETERSON, *J. Mater. Sci.*, 2006, 41, (13), 4251–4258

The partially oxidised (PO) salts of the bis(oxalato)platinate(II) (1) and tetra(cyano)platinate(II) complexes were electrochemically prepared in glass capillary templates (900 nm in length), as well as through porous anodic Al oxide templates with pore diameters of 200 nm and 20 nm. The PO (1) polymers have significant flexibility on the nanoscale. The formation of the PO polymers could be directed by varying the positions and the number of electrodes.

Multiple Additions of Palladium to C₆₀

O. LOBODA, V. R. JENSEN and K. J. BØRVE, *Fullerenes, Nanotubes, Carbon Nanostruct.*, 2006, 14, (2–3), 365–371

DFT calculations on exohedral Pd_{*n*}C₆₀ show that the Pd–fullerene bond energy remains essentially constant for $n = 1–6$. A Pd₂(η²-C₆₀) structure with the two metal atoms bridging over a six-membered ring is the most stable arrangement of two Pd atoms on the surface of C₆₀. Entropy considerations suggest that isolated atoms and weakly bonded metal aggregates may exist in equilibrium. Binding of Pd atoms to the fullerene is preferred over Pd dimerisation.

Fluorous Nanodroplets Structurally Confined in an Organopalladium Sphere

S. SATO, J. IIDA, K. SUZUKI, M. KAWANO, T. OZEKI and M. FUJITA, *Science*, 2006, 313, (5791), 1273–1276

Arrow-shaped N-donor ligands with perfluoroalkyl tails self-assembled with Pd ions in DMSO to form a shell in which the fluorinated chains (1) are directed inward toward the centre. Crystallographic analysis confirmed the rigid shell framework and amorphous interior. By varying the lengths of (1), the shell size could be tuned to encapsulate a liquid-like, disordered phase of ~ 2–6 perfluorooctane molecules.

Crystal Structure and Infrared Spectroscopy of Bis(2-hydrazinopyridine)palladium(II) Chloride and its Isotopomers

P. DROZDZEWSKI, M. MUSIALA and M. KUBIAK, *Aust. J. Chem.*, 2006, 59, (5), 329–335

Reaction of PdCl₂ with 2-hydrazinopyridine (hypy) in DMF gave [Pd(hypy)₂]Cl₂, whereas it recrystallised from MeOH to give [Pd(hypy)₂]Cl₂·2MeOH (1). Single crystal X-ray analysis of (1) revealed the planar structure of the metal vicinity and *trans*-orientation of the ligands, chelating the Pd through amine and pyridine N atoms. IR spectroscopy and DFT modelling were used to study the vibrations of [Pd(hypy)₂]²⁺.

Preparation of Five- and Six-Coordinate Aryl(hydrido) Iridium(III) Complexes from Benzene and Functionalized Arenes by C–H Activation

H. WERNER, A. HÖHN, M. DZIALLAS and T. DIRNBERGER, *Dalton Trans.*, 2006, (21), 2597–2606

Reaction of the *in situ* generated cyclooctene Ir(I) derivative $trans\text{-}[\text{IrCl}(\text{C}_8\text{H}_{14})(\text{P}t\text{Pr}_3)_2]$ with benzene at 80°C gave a mixture of $[\text{IrH}_2(\text{Cl})(\text{P}t\text{Pr}_3)_2]$ and $[\text{IrH}(\text{C}_6\text{H}_5)(\text{Cl})(\text{P}t\text{Pr}_3)_2]$ in the ratio of ~ 1:2. $\text{C}_6\text{H}_5\text{X}$ (X = Cl, F), $\text{C}_6\text{H}_4\text{F}_2$ and $\text{C}_6\text{H}_4\text{F}(\text{CH}_3)$ also reacted by C–H activation to afford $[\text{IrH}(\text{C}_6\text{H}_4\text{X})(\text{Cl})(\text{P}t\text{Pr}_3)_2]$, $[\text{IrH}(\text{C}_6\text{H}_3\text{F}_2)(\text{Cl})(\text{P}t\text{Pr}_3)_2]$ and $[\text{IrH}\{\text{C}_6\text{H}_3\text{F}(\text{CH}_3)\}(\text{Cl})(\text{P}t\text{Pr}_3)_2]$, respectively. The formation of isomeric mixtures was detected by ^1H , ^{13}C , ^{19}F and ^{31}P NMR spectroscopy.

Oligo(U-terpyridines) and Their Ruthenium(II)

Complexes: Synthesis and Structural Properties

A. WINTER, J. HUMMEL and N. RISCH, *J. Org. Chem.*, 2006, 71, (13), 4862–4871

The domino reaction of tetrahydroquinolinone with bisiminium salts gave rigid U-shaped substituted terpyridines, bis(U-terpyridines) (L). Treatment of L with $[(\text{tpy})\text{RuCl}_3]$ afforded $[(\text{tpy})\text{Ru}(\text{L})\text{Ru}(\text{tpy})]^{4+}$. A star-shaped tris(U-terpyridine) and $[\{(\text{tpy})\text{Ru}\}_3(\text{tris}(\text{U-terpyridine}))]^{6+}$ were also obtained. The Ru complexes were light-emitting upon excitation at 340 nm, with broad emission maxima between 400–500 nm.

ELECTROCHEMISTRY

Electrochemical Polymerization of Acetylene on Rh Electrodes Probed by Surface-Enhanced Raman Spectroscopy

G.-K. LIU, B. REN, D.-Y. WU, J.-M. LIN, R.-A. GU and Z.-Q. TIAN, *J. Electroanal. Chem.*, 2006, 594, (2), 73–79

The electrochemical behaviours of C_2H_2 (1) on a roughened Rh electrode in 0.1 M HClO_4 were studied by a combination of CV and SERS. On both roughened and smooth Rh surfaces, a clear loop in the cyclic voltammogram was present in the negative potential region. However, a surface species Raman signal was only observed for the roughened Rh surface. The resemblance of the detected signal to that of polyacetylene indicates the occurrence of polymerisation of (1) at potentials more negative than -0.3 V.

Preparation and Characterization of $\text{RuO}_2\text{-IrO}_2\text{-SnO}_2$ Ternary Mixtures for Advanced Electrochemical Technology

L. VAZQUEZ-GOMEZ, S. FERRO and A. DE BATTISTI, *Appl. Catal. B: Environ.*, 2006, 67, (1–2), 34–40

The title coatings (1) were prepared by a thermal decomposition method, requiring an oxidative pyrolysis step of precursor salt deposits at 480°C. The coating compositions were: $\text{Ir}_x\text{Ru}_{0.34-x}\text{Sn}_{0.66}\text{O}_2$ (x nominal values = 1.7, 3.7, 7.3, 11.6, 17.9, 23.3, 28.4, 31.6 and 33.5%). (1) were deposited on Ti supports. A compromise between catalytic properties and wear resistance was found with coatings containing ~ 20% of Ir (hence ~ 15% of Ru).

Electrochemical Capacitors Based on Electrodeposited Ruthenium Oxide on Nanofibre Substrates

Y. R. AHN, M. Y. SONG, S. M. JO, C. R. PARK and D. Y. KIM, *Nanotechnology*, 2006, 17, (12), 2865–2869

Electrodeposition of RuO_2 on electrospun TiO_2 nanorods using CV increased the capacitance of RuO_2 . This is attributed to the large surface areas of the nanorods. The electrode deposited from 0.25–1.45 V (with respect to Ag/AgCl) exhibited a specific capacitance of 534 F g^{-1} after deposition for 10 cycles with a scan rate of 50 mV s^{-1} . The structural H_2O content in RuO_2 varied depending on the deposition potential range. Higher amounts of structural H_2O in RuO_2 increased the charge storage capability.

ELECTRODEPOSITION AND SURFACE COATINGS

Catalyst-Enhanced Chemical Vapor Deposition of Palladium-Platinum Bilayer Films on Polyimide

J. ZHENG, J. ZHOU, K. YU, X. GE and S. YU, *Chin. J. Catal.*, 2006, 27, (6), 465–467

Catalyst-enhanced CVD of Pt, Pd and Pd-Pt bilayer films on polyimide using N_2 and O_2 as the carrier gases was studied at 220–300°C under reduced or normal pressure. The films were deposited at a rate of 70–80 nm h^{-1} . When a mixture of Pt complex and Pd complex was used as precursors in the same chamber, only Pt was deposited. Sequential deposition of Pd and Pt metals formed a Pd-Pt bilayer.

Tarnishing Resistance of Silver-Palladium Thin Films

M. DORRIOT-WERLÉ, O. BANAKH, P.-A. GAY, J. MATTHEY and P.-A. STEINMANN, *Surf. Coat. Technol.*, 2006, 200, (24), 6696–6701

Thin Ag-Pd films (1) were deposited by magnetron cosputtering from Pd and Ag targets. Increasing Ar gas pressure and substrate temperature caused a drastic decrease of the specular reflectivity of (1). At constant deposition conditions the reflectivity of (1) decreased with increasing Pd content. Sulfidation test results indicated an improvement of tarnishing resistance of (1) with increasing Pd content.

APPARATUS AND TECHNIQUE

Hydrogen Isotope Separation by Permeation through Palladium Membranes

M. GLUGLA, I. R. CRISTESCU, I. CRISTESCU and D. DEMANGE, *J. Nucl. Mater.*, 2006, 355, (1–3), 47–53

Based on an experimentally verified mathematical model, a computational study was performed to show the net isotope effects in permeate and bleed flows when feeding a Pd permeator with H isotope mixtures under different feed and permeate pressures. The feasibility of H isotope permeation as a method for separation is discussed with regard to the process control for a single permeator or a cascade.

Improved Photocatalytic Deposition of Palladium Membranes

X. LI, Y. FAN, W. JIN, Y. HUANG and N. XU, *J. Membrane Sci.*, 2006, 282, (1–2), 1–6

A TiO₂ support was immersed into a photocatalytic deposition bath (PdCl₂, HCl, EDTA, deionised H₂O). Then the TiO₂ membrane was lifted out, and subsequently a thin liquid film was formed on the TiO₂ surface. The liquid film-coating was directly irradiated at room temperature. A tubular Pd membrane (0.4 μm thickness) was synthesised, which exhibited high H₂ permeance of 4.8×10^{-6} mol m⁻² s⁻¹ Pa⁻¹ and H₂/N₂ selectivity of 120 at 704 K.

HETEROGENEOUS CATALYSIS

Naphthalene Oxidation over Vanadium-Modified Pt Catalysts Supported on γ-Al₂O₃

E. N. NDIFOR, T. GARCIA and S. H. TAYLOR, *Catal. Lett.*, 2006, 110, (1–2), 125–128

Pt/γ-Al₂O₃ catalysts (1) modified by V were prepared and then tested for the complete oxidation of naphthalene. Only 0.5% V promoted the activity of 0.5% Pt/γ-Al₂O₃. The enhancement is related to the presence of a more easily reducible V species coupled with the enhanced number of surface Pt sites. The reduced activity of (1) with higher V content (1–12%) is attributed to the presence of crystalline V₂O₅.

Pd and Pt Catalysts Supported on Carbon-Coated Monoliths for Low-Temperature Combustion of Xylenes

A. F. PÉREZ-CADENAS, F. KAPTEIJN, J. A. MOULIJN, F. J. MALDONADO-HÓDAR, F. CARRASCO-MARÍN and C. MORENO-CASTILLA, *Carbon*, 2006, 44, (12), 2463–2468

C-coated monoliths (1) were prepared from polyfurfuryl alcohol coated cordierite structures. Pd and Pt catalysts were obtained by equilibrium impregnation of (1). The catalysts were pretreated in H₂ at 300°C. The Pt catalysts were more active in xylene combustion. Complete combustion was reached at 150–180°C with a total selectivity to CO₂ and H₂O. Combustion of *m*-xylene was easier than *p*-xylene.

A Selective Synthesis of Acetic Acid from Syngas over a Novel Rh Nanoparticles/Nanosized SiO₂ Catalysts

W.-M. CHEN, Y.-J. DING, D.-H. JIANG, T. WANG and H.-Y. LUO, *Catal. Commun.*, 2006, 7, (8), 559–562

Microemulsions of polyethyleneglycol-*p*-nonylphenyl ether in cyclohexane were prepared by injecting aqueous RhCl₃ solutions. Rh–N₂H₄ nanoparticles (1) were formed by addition of hydrazine hydrate. (1) were separated from the oil phase. After the supernatant was decanted, (1) were washed, dried and calcined. Rh nanoparticles/nanosized SiO₂ (2) was prepared by grinding the resultant Rh nanoparticles with nanosized SiO₂. The total selectivity of acetic acid and ethyl acetate in the oxygenate products of CO hydrogenation on (2) reached 74.8%.

Effect of Carbon Nanotubes on Activity of Rh-Ce-Mn/SiO₂ Catalyst for CO Hydrogenation to Oxygenates

L. HUANG, W. CHU, J. HONG and S. LUO, *Chin. J. Catal.*, 2006, 27, (7), 596–600

The catalytic performance of C nanotubes (CNTs)-promoted Rh-Ce-Mn/SiO₂ (1) for CO hydrogenation to oxygenates was studied. The CNTs improved the dispersion of Rh and increased the active components on the surface of (1). The amount of strongly adsorbed H₂ or CO on the surface of (1) was increased. The results of CO hydrogenation showed that the CNTs enhanced the activity of (1).

Ruthenium Hydroxide on Magnetite as a Magnetically Separable Heterogeneous Catalyst for Liquid-Phase Oxidation and Reduction

M. KOTANI, T. KOIKE, K. YAMAGUCHI and N. MIZUNO, *Green Chem.*, 2006, 8, (8), 735–741

Ru(OH)_x/Fe₃O₄ (1) can be used as the catalyst for: (a) aerobic oxidation of alcohols; (b) aerobic oxidation of amines; and (c) reduction of carbonyl compounds to alcohols using 2-propanol as a H donor. Separation of (1) from the product(s) was easily achieved with a permanent magnet, and > 99% of (1) could be recovered for each reaction. (1) recovered after these reactions could be reused.

HOMOGENEOUS CATALYSIS

A User-Friendly, All-Purpose Pd-NHC (NHC = N-Heterocyclic Carbene) Precatalyst for the Negishi Reaction: A Step Towards a Universal Cross-Coupling Catalyst

M. G. ORGAN, S. AVOLA, I. DUBOVYK, N. HADEI, E. A. B. KANTCHEV, C. J. O'BRIEN and C. VALENTE, *Chem. Eur. J.*, 2006, 12, (18), 4749–4755

The air stable, highly active, precatalyst PEPPSI-IPr (PEPPSI = pyridine-enhanced precatalyst preparation, stabilisation and initiation; IPr = diisopropylphenylimidazolium derivative) can be used with PdCl₂ for the Negishi reaction. Organohalides and routinely used pseudohalides were excellent coupling partners. General laboratory techniques are employed for all of the reactions.

Open-Vessel Microwave-Promoted Suzuki Reactions Using Low Levels of Palladium Catalyst: Optimization and Scale-Up

N. E. LEADBEATER, V. A. WILLIAMS, T. M. BARNARD and M. J. COLLINS, *Org. Process Res. Dev.*, 2006, 10, (4), 833–837

Suzuki couplings using low Pd catalyst concentrations (1–5 ppm Pd) with microwave heating have been transferred from sealed-vessel to open-vessel reaction conditions. The procedure is scalable from the mmol to the 1 mol scale. The reactions can be performed in air and are run using H₂O/EtOH as the solvent system. The couplings are complete within 20 min of heating at reflux.

Highly Enantioselective Fluorination Reactions of β -Ketoesters and β -Ketophosphonates Catalyzed by Chiral Palladium Complexes

Y. HAMASHIMA, T. SUZUKI, H. TAKANO, Y. SHIMURA, Y. TSUCHIYA, K. MORIYA, T. GOTO and M. SODEOKA, *Tetrahedron*, 2006, 62, (30), 7168–7179

Using chiral Pd enolates as key intermediates, highly enantioselective fluorination reactions ($\leq 98\%$ ee) of β -ketoesters and β -ketophosphonates have been carried out. These reactions were carried out in alcoholic solvents without any need to exclude air and H₂O. Transformation of the fluorinated products was successfully achieved.

Nitrogen Ligand-Containing Rh Catalysts for the Polymerization of Substituted Acetylenes

I. SAEED, M. SHIOTSUKI and T. MASUDA, *J. Mol. Catal. A: Chem.*, 2006, 254, (1–2), 124–130

Rh complexes having a phenoxy-imine ligand, a β -diiminate ligand, and NH₃ ligands were used in the polymerisation of substituted acetylenes. Polymers in moderate to high yields with high molecular weights were afforded. A cocatalyst was not required in these systems in contrast to [Rh(nbd)Cl]₂ and [Rh(cod)Cl]₂. In the case of the phenoxy-imine catalysts, the nbd-bearing one was more active than the cod-bearing counterpart, while the opposite trend was observed for the β -diiminate catalysts.

The Hydrogenation of Cinnamaldehyde by Supported Aqueous Phase (SAP) Catalyst of RhCl(TPPTS)₃: Selectivity, Kinetic and Mass Transfer Aspects

K. NUTHITIKUL and J. M. WINTERBOTTOM, *Chem. Eng. Sci.*, 2006, 61, (18), 5944–5953

The hydrogenation of *trans*-cinnamaldehyde was catalysed by RhCl(TPPTS)₃/SiO₂ (1) (TPPTS = trisodium salt of tris(*m*-sulfophenyl)phosphine). The hydrogenation is selective at the C=C bonds in cinnamaldehyde giving hydrocinnamaldehyde as the main product. High selectivity (99.9%) was achieved by employing a low initial concentration of cinnamaldehyde. Optimum H₂O content of (1) giving maximum activity occurred when the pore volume of the supports was completely filled with H₂O.

Isomerizing-Hydroboration of the Monounsaturated Fatty Acid Ester Methyl Oleate

K. Y. GHEBREYESSUS and R. J. ANGELICI, *Organometallics*, 2006, 25, (12), 3040–3044

[Ir(cyclooctene)₂Cl]₂/dppe catalysed the hydroboration of methyl oleate (18:1) with pinacolborane to give a product (1) in which the boronate ester group is in the terminal (C18) position. The formation of (1) shows that the catalyst promotes both the isomerisation of the double bond from the 9,10-position of 18:1 to the terminal position and the selective hydroboration of this isomer to give (1) in 45% yield. This tandem reaction is claimed to have the potential to be capable of converting all isomers of 18:1 into (1).

FUEL CELLS

Preparation of High Catalyst Utilization Electrodes for Polymer Electrolyte Fuel Cells

J. M. SONG, S. SUZUKI, H. UCHIDA and M. WATANABE, *Langmuir*, 2006, 22, (14), 6422–6428

Pt/C black (high surface area) and Nafion ionomer solution were heated in an autoclave at 200°C, followed by quenching to form an ink (1). A cathode prepared with (1) exhibited high catalyst utilisation and improved gas diffusivity. The autoclave treatment promoted an effective introduction of Nafion ionomer into primary pores of the Pt/C black agglomerates.

Characteristics of a Platinum Black Catalyst Layer with Regard to Platinum Dissolution Phenomena in a Membrane Electrode Assembly

K. YASUDA, A. TANIGUCHI, T. AKITA, T. IOROI and Z. SIROMA, *J. Electrochem. Soc.*, 2006, 153, (8), A1599–A1603

Pt dissolution and precipitation in a PEM of a MEA was studied using a potential holding experiment at 1.0 V *vs.* a reversible H electrode and HRTEM. The electrochemically active surface area decreased depending on the holding time, and Pt deposition was observed in the PEM near a cathode catalyst layer. However, Pt dissolution and deposition out of the catalyst layer were greatly reduced when a Pt black electrode was employed. Using a double-layered catalyst layer, Pt redeposited on the Pt black surface.

Characterization of Membrane Electrode Assembly for Fuel Cells Prepared by Electrostatic Spray Deposition

M. UMEDA, S. KAWAGUCHI and I. UCHIDA, *Jpn. J. Appl. Phys., Part 1*, 2006, 45, (7), 6049–6054

A Pt/C MEA prepared by electrostatic spray deposition was installed in a fuel cell and demonstrated as high a performance as that of a MEA prepared by air-spraying. The cross-sectional morphology of the catalyst layer explained the coupling strength in a peel-off test and the dependence of current-voltage characteristics on catalyst layer thickness.

Synthesis, Characterization, and Electrocatalytic Activity of PtBi and PtPb Nanoparticles Prepared by Borohydride Reduction in Methanol

C. ROYCHOWDHURY, F. MATSUMOTO, V. B. ZELDOVICH, S. C. WARREN, P. F. MUTOLO, M. BALLESTEROS, U. WIESNER, H. D. ABRUÑA and F. J. DISALVO, *Chem. Mater.*, 2006, 18, (14), 3365–3372

PtPb and PtBi nanoparticles displayed enhanced electrochemical activity toward formic acid and MeOH oxidation as compared with those of Pt and PtRu nanoparticles. The electrocatalytic activity of the PtPb nanoparticles was studied as a function of sonication time of the catalyst ink, and morphology changes were followed by SEM. The activity of the PtPb catalyst initially increased with sonication time, peaked at 6 h, and then decreased.