of current literature on the platinum metals and their alloys

**PROPERTIES**

Size Effects on the Thermal Conductivity of Polycrystalline Platinum Nanofilms


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.

**CHEMICAL COMPOUNDS**

Growth and Characterization of Partially Oxidized Platinum Polymers in Nanoscale Templates


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.

**Surface Segregation and Homogenization of Pd<sub>70</sub>Ag<sub>30</sub> Alloy Nanoparticles**


In this study Pd<sub>70</sub>Ag<sub>30</sub> nanoparticles (1) with the smallest size and the highest homogeneity were prepared using the strong reducing agent NaBH<sub>4</sub>. 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 N<sub>2</sub>H<sub>4</sub> was intermediate between those of the other two samples.

**Fluorous Nanodroplets Structurally Confined in an Organopalladium Sphere**


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**


Reaction of PdCl<sub>2</sub> with 2-hydrazinopyridine (hypy) in DMF gave [Pd(hypy)]<sub>2</sub>Cl<sub>2</sub>, whereas it recrystallised from MeOH to give [Pd(hypy)]<sub>2</sub>Cl<sub>2</sub>·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)]<sup>2+</sup>.
Preparation of Five- and Six-Coordinate Aryl(hydrido) Iridium(III) Complexes from Benzene and Functionalized Arenes by C–H Activation


Reaction of the **in situ** generated cyclooctene Ir(I) derivative trans-[IrCl(C8H14)(PPr3)2] with benzene at 80ºC gave a mixture of [Ir(C6H5Cl)(PPr3)2] and [Ir(C6H4FCl)(PPr3)2] in the ratio of ~ 1:2. C6H5X (X = Cl, F), C6H4F2 and C6H4F(CH3) also reacted by C–H activation to afford [IrH2(Cl)(PPr3)] and [IrH(C6H4FCl)(Cl)(PPr3)] respectively. The formation of isomeric mixtures was detected by 1H, 13C, 19F and 31P NMR spectroscopy.

ELECTROCHEMISTRY

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


Catalyst-enhanced CVD of Pt, Pd and Pd-Pt bilayer films on polyimide using N2 and O2 as the carrier gases was studied at 220–300ºC 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


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. Sulfdation 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


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 means for separation is discussed with regard to the process control for a single permeator or a cascade.
Improved Photocatalytic Deposition of Palladium Membranes


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


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


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 attained 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


Microemulsions of polyethylene glycol-p-nonylphenyl ether in cyclohexane were prepared by injecting aqueous RhCl₃ solutions. Rh-N₃H₂ 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-GeMn/SiO₂ Catalyst for CO Hydrogenation to Oxygenates


The catalytic performance of C nanotubes (CNTs)-promoted Rh-Ge-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)₃/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


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 pseudo-halides 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


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 \(\beta\)-Ketoesters and \(\beta\)-Ketophosphonates Catalyzed by Chiral Palladium Complexes


Using chiral Pd enolates as key intermediates, highly enantioselective fluorination reactions (\(\geq 98\%\) ee) of \(\beta\)-ketoesters and \(\beta\)-ketophosphonates have been carried out. These reactions were carried out in alcoholic solvents without any need to exclude air and H\(_2\)O. 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, 

Rh complexes having a phenoxy-imine ligand, a \(\beta\)-diiminate ligand, and NH\(_3\) 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]] and [Rh(cod)[Cl]]. 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 \(\beta\)-diiminate catalysts.

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

K. Nuthitikul and J. M. Winterbottom, 

The hydrogenation of trans-cinnamaldehyde was catalysed by RhCl(TPPTS)\(_2\)SiO\(_3\) (1) (TPPTS = trisodium salt of tris(m-sulphophenyl)phosphine). The hydrogenation is selective at the \(\text{C}=\text{C}\) bonds in cinnamaldehyde giving hydrocinnamaldehyde as the main product. High selectivity (99.9\%) was achieved by employing a low initial concentration of cinnamaldehyde. Optimum H\(_2\)O content of (1) giving maximum activity occurred when the pore volume of the supports was completely filled with H\(_2\)O.

Isomerizing-Hydroboration of the Monounsaturated Fatty Acid Ester Methyl Oleate

K. Ghebreyesus and R. J. Angelici, 

[Ir(cyclooctene)][Cl]/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 200ºC, 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. Iorio and Z. Siroma, 

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, 

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

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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.