ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Grain Growth in Ultrathin Films of CoPt and FePt
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Thin films (10 nm) of CoPt and FePt sputter deposited on oxidised Si wafers have been characterised using TEM. A rapid growth stage concurrent with the formation of a [111] fibre texture was observed to occur within 5–10 minutes of annealing, followed by a much slower growth stage after the fibre texturing was well advanced. Differences in grain growth rate and ultimate grain size were observed to be dependent on heating rate.

The Effect of Platinum Additions on the Oxidation of Directionally-Solidified Ni-Cr-Al-Y-Cr2Al, Alloys at 1,100 and 1,200°C

The effects of 2 wt.% Pt additions on the oxidation of the title alloys were investigated under isothermal and thermal cycling conditions. At 1100°C, the addition of Pt favoured the formation of a continuous Al2O3 scale over primary carbides intersecting the alloy surface. The scale remained substantially adherent after isothermal oxidation, but lifted and cracked on thermal cycling. At 1200°C, an external Al2O3 scale formed initially, but spalled extensively after short times under both isothermal and thermal cycling conditions.

Novel Hydrogen Sensors Using Evanescent Microwave Probes

Evanescence microwave probes (EMP) were used to detect deflections in a Pd-coated cantilever and to quantify the amount of stress and the resistivity change in the Pd film as a function of H2 concentration. The stress was 5.26–8.59 × 10−9 Pa for 0.5–1.4% H2 concentration at room temperature, which is about 3 times larger than that found in bulk Pd for the same H2 concentrations. The resistivity of the Pd films changed by 13.5% at 3.0% H2 giving 18% change in the EMP signal. H2 concentrations of 0.014% could be detected by the EMP.

Alloying Elements Partitioning in TiAl-Ru Intermetallic Alloys

The solute partitioning behaviour in two phase α + γ Ti-48 at. % Al-0.5 at. % Ru alloys was investigated using atom-probe field-ion microscopy. Ru was depleted in α and interstitial elements were localised in the α phase. The degree of localisation for interstitials is much more significant than for substitutional elements.

Infrared Spectra and Density Functional Calculations of RuCOx, OsCOx, Ru(CO)x, Os(CO)x, Ru(CO)x and Os(CO)x (x = 1–4) in Solid Neon

Laser ablated Ru and Os atoms were co-deposited with CO (0.05–0.2%) during condensation in excess Ne. M(CO)3 (M = Os, Ru; x = 1–5) were formed during deposition or on annealing, while M(CO)x (x = 1–4) were formed by electron capture. MCO+ were produced by metal cation reactions. IR characterisations were recorded. Density functional calculations predicted these frequencies within 1% and the isotopic shifts for different C-O stretching modes within averages of 1–2 cm−1.

CHEMICAL COMPOUNDS

Luminescence and Aggregation Studies of Hexanuclear Platinum–Copper Acetylide Complexes. Crystal Structure of the Luminescent Metal–Metal Bonded Dimer [Pt2Cu,(C=CPh)l2]3-

[Sr(C≡CPh)3]2-Pt2Cu,(C≡CPh)l2] (1) was synthesised by the reaction of [NaBu3][Pt(C≡CPh)3] (2) with [Cu(MeCN)][PF6] in acetone. (1) was shown to exist in the dimeric form only in concentrated solution through a Pt-Pt bonding interaction. The shift in the v(C≡C) absorption to a lower wavenumber in (1) than in (2) was indicative of a π-bonding mode of the acetylen ligands.

Palladium and Platinum Dithiocarbamato Complexes Containing Mono- and Diamines

[M(DMDT)X]3+ (M = Pd, Pt; DMDT = MeNCS); X = Cl, Br) were reacted with amines (Am) (Py, pyridine; Ppa, p-propylamine; Cba, cyclobutylamine; Dap, 1,3-diaminopropane; Eo, ethylenediamine) to give M(DMDT)X3 (I = Pd; Ppa, Cba, Dap, Eo, Am). [M(DMDT)(I)X]3 (I = Pd, Pt; Dap, Eo, Am). TGA data suggest a particular behaviour for Pd-Pra and Pd-Cba, with the formation of low stoichiometry intermediates Pd(DMDT)2AmX3.
Design of Novel Hexametallic Cartwheel Molecules from Persubstituted Benzene Compounds

Nanosized hexametallic Pd species with persubstituted benzenes C,[3,5-(CH,Y),C,H??], PPh, SPh) were synthesised. The molecular structure of 2186-2188

Design of Novel Hexametallic Cartwheel Molecules
ed benzenes C,


Using CpIr(CO)2 as a 2e donor ligand, the metal complexes Cp(O)Ir(2e)(CO)(X)z were prepared and characterised. The crystal structures of (1), (2) and (3) all contain an unbridged metal-metal bond. With the exception of (2), all the complexes dissociate in solution at room temperature, some of them rapidly. CpIr(CO)2 is a weak ligand, comparable in ligating ability to Os(CO)2.

Development of Carbon-Metal Oxide Supercapacitors from Sol-Gel Derived Carbon-Ruthenium Xerogels

Sol-gel high surface area C-Ru xerogel composites (1) were prepared from carbonised resorcinol-formaldehyde resins containing RuOx-xH2O. A very high specific capacitance of 256 F g–1 (single electrode) was obtained from (1) with 14 wt.% Ru, which corresponds to > 50% utilisation of the Ru. (1) also showed no change in electrochemical capacitance after 2000 charge/discharge cycles, indicating that (1) was very stable and the redox reactions associated with the RuOx were completely reversible.

PHOTOCONVERSION

Viologen-linked porphyrin (1) and viologen-free porphyrin (2) were synthesised and their Pt-loaded Langmuir-Blodgett (LB) films (3) prepared. Steady photoinduced H2 evolution was observed using (3) under steady-state irradiation in the presence of EDTA as a sacrificial electron donor. The rate of H2 production using (1) was larger than for (2). H2 evolution continued for longer using (1). In LB film with (1), the degradation via the reduced form of porphyrin is repressed.

Photoluminescence of Trimeric Palladium(II) Acetate in Solution

Pd(acetate), (1) shows photoluminescence in benzene at Amax = 475 nm (fluorescence) and 595 nm (phosphorescence). The longer wavelength emission is quenched in the presence of air while the shorter wavelength luminescence is hardly affected by O2. The emission of (1) is related to its trimeric structure and disappears when K(acetate) is added. The luminescence originates from the de* → pσ excited state, involving metal-metal interaction in the triangular (Pd3+) moiety.

Electrochemistry
Nickel Electrowinning Using a Pt Catalysed Hydrogen-Diffusion Anode. Part II: Batch Tank with a Sulphate Bath

A Pt catalysed H2-diffusion anode was used for Ni electrowinning from a NiSO4 bath with a stainless steel/Ni cathode. The anode comprised a C cloth coated with ~ 5 mg cm–2 of C black + PTFE with 10 wt.% Pt. For Ni2+ contents of 50–125 g l–1, current efficiencies > 93% were found. Energy costs increased linearly as current density increased from 10–50 mA cm–2, but at values much lower than those from a conventional Pb anode.
Luminescent Nafion Membranes Dyed with Ruthenium(II) Complexes as Sensing Materials for Dissolved Oxygen


Indicator layers for luminescence optosensing of O₂ showing no dye leaching and avoiding the use of adsorbing materials were developed by using [Ru(t3f)]²⁺ complexes (L = 2,2'-bipyridine, 1,10-phenanthroline, 5-octadecanamide-1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline (dip)) immobilised in Nafion. The O₂ sensitivity of [Ru(dip)]²⁺ dipped in MeOH was independent of the Ru(II) loading and Nafion counterion. Highly O₂-sensitive luminescent membrane, for monitoring in organic solvents, H₂O and the gas phase, was prepared on immobilising [Ru(dip)]²⁺ in 178 μm thick Nafion.

ELECTRODEPOSITION AND SURFACE COATINGS

Excimer Lamp-Induced Decomposition of Platinum Acetylacetonate Films for Electroless Copper Plating


Photo-induced decomposition of Pt acetylacetonate films (1) was achieved using an excimer VUV source of 172 nm radiation. VUV irradiation of non-catalytic substrates coated with (1) formed Pt metal, which is an activator for an electroless Cu plating process. The photodecomposition rate of Pt acetylacetonate was found to be strongly dependent upon the UV dose, the chamber pressure during irradiation and exposure time.

X-Ray Photoelectron Spectroscopy Study of Pt-Oxide Thin Films Deposited by Reactive Sputtering Using O₂/Ar Gas Mixtures


Pt-oxide thin films (1) were obtained by reactive r.f. magnetron sputtering of Pt at a relatively high partial pressure of O₂. XRD indicated that (1) have an amorphous structure. From XPS, it was found that chemical shifts of the Pt 4f peaks occur, and the amount of energy shifts are 1.0 and 2.1 eV. After comparison with known data, it was concluded that (1) are composed of PtO grains and intermediate mixtures of PtO and PtO₂.

Electroless Plating of Metals onto Carbon Nanotubes Activated by a Single-Step Activation Method


Oxidised C nanotubes were activated with Pd-Sn catalytic nuclei. A HCl accelerator was used to preferentially dissolve the protective layer, exposing more surface area of the Pd-Sn nuclei. These activated nanotubes were used as precursors for Ni- and Pd-coated nanotubes via electroless plating. Metal deposition occurs at the catalytic sites. The deposited clusters of metal atoms then catalyse further metal deposition on the tube surface.

Effect of the Deposition Temperature on the Properties of Iridium Thin Films Grown by Means of Pulsed Laser Deposition


Pulsed laser deposited Ir thin films (1) were obtained by ablating an Ir target with a KrF excimer laser. At the deposition temperatures of 20–600°C, (1) are polycrystalline with a preferred (111) orientation, especially at 200–500°C. The average grain size of (1) continuously increased from ~ 10 to 30 nm and the stress changed drastically from highly compressive to tensile, as the deposition temperature was raised. The room temperature resistivity of (1) gradually decreases in the range 20–400°C and stabilises for higher temperatures. (1) with the lowest resistivity and a nearly zero stress level can be grown at 400°C.
Fabrication of Defect-Free Pd/α-Al2O3 Composite Membranes for Hydrogen Separation


A thin film Pd/α-Al2O3 composite membrane (1), where Pd thickness is 10.3 μm, was fabricated by electroless plating combined with osmosis. The H2 permeation performance of (1) was investigated using pure H2 at various temperatures from 320–577°C. H2 effects on the surface of (1) had an influence on H2 permeation, so that the H2 permeation performance diverged slightly from Sievert’s law. The apparent activation energy for (1) was 12.3 kJ mol−1 at 320–577°C. Both a sweep gas of N2 and a higher total feed flow rate improved H2 permeation through (1).

Composition Control and Hydrogen Permeation Characteristics of Sputter Deposited Palladium-Silver Membranes


Submicron thick continuous Pd-Ag films (1) were deposited by sputtering on mesoporous γ-Al2O3 from a target composed of 75% Pd and 25% Ag. (1) were tested in a multigas permeation system for H2 permeance and H2 selectivity over He. H2 permeance for (1) was found to be 3 × 10−4 to 1 × 10−2 mol m−2 s−1 Pa and H2:He selectivities were in the range 4–4000, depending mainly on the Ag concentration and microstructure of (1).

HETEROGENEOUS CATALYSIS
Extraordinarily Effective Promotion by Sodium in Emission Control Catalysis: NO Reduction by Propene over Na-Promoted Pt/γ-Al2O3


The catalytic activity and selectivity of Pt/γ-Al2O3, for the reduction of NO by propene, was found to be promoted extremely strongly by Na at 470–770 K. Rate increases of two-orders of magnitude were achievable, with the selectivity towards N2 was improved from 15% over Na-free unpromoted Pt to >95% over 4.18 wt.% Na-promoted Pt.

Treatment of Combined Bleach Plant Effluents via Wet Oxidation over a Pd-Plt- Ce/Alumina Catalyst


Pd-Plt-Ce(Alumina) (1) shows promising activity over traditional Fe3O4, ZnO-type, oxidation catalysts for the treatment of bleach plant effluents. At 443 K and 1.5 MPa in a slurry reactor, 65% total organic carbon (TOC) and 99% colour were removed after a 3 h treatment, while only 10% TOC and 79% colour reduction were achieved without catalyst under the same experimental conditions. Cheap ferrous-based alloy may be used as the construction material for the process equipment. (1) may also be applied to the treatment of other organic wastes.

Dowex® 1-Supported PtCl, Ion Pair as a Recycle Hydrogenation Catalyst


Polystyrene-supported ion pairs formed from PtCl and Dowex® 1 anion exchangers in EtOH, were found to be sufficiently stable under H2 to function as efficient and recyclable catalysts for the hydrogenation of various alkenes and other unsaturated compounds at <35°C. In the hydrogenation of 1-decene, the intraparticle diffusion of the substrate contributed to the overall rate of the reaction. XPS identified Pt(II) and Pt(IV) species in the reaction mixture. No Pt(0) was traced.

Water-Soluble Colloidal Adams Catalyst: Preparation and Use in Catalysis


The hydrolysis/condensation of PtCl6 or H2PtCl6 under basic conditions in the presence of carboxyl or sulfo-betaine stabilisers was shown to be a simple route to preparing H2O-soluble, stable, nanosized colloidal PtO6. The nanoparticles can be immobilised on neutral Al2O3 with the formation of highly active heterogeneous (pre)catalysts. This route was extended to the fabrication of bimetallic PtRuO6 systems. Such H2O-soluble mixed metal oxides have potential as chemical (pre)catalysts in organic transformations and electrocatalysts in fuel cells.

Pd-Cu Supported on Anionic Polymers – Promising Catalysts for Removal of Nitrates from Drinking Water


Bimetallic catalyst (1) with 2 wt.% Pd and 0.5 wt.% Cu, deposited on microporous anionic resin Dowex 50 W X 4, was able to reduce the NO3 content in H2O from 100 to 47 mg l−1 after a 4 h treatment (1 mmol Pd per litre of H2O) at ambient temperature and atmospheric pressure with vigorous stirring of the mixed mixture. (1) kept its activity for 2 further cycles. The catalyst, regenerated with a dilute mineral acid, had only slightly lower activity and selectivity for N2 formation than the original catalyst.

Methane Combustion on Sol-Gel Rh/ZrO2-SiO2 Catalysts


Studies of Rh/ZrO2-SiO2 catalysts (1) prepared by the impregnation of mixed ZrO2-SiO2 (by the sol-gel method) showed that the specific area and porosity depended strongly on the pH of the gelation. When Zr(acac)4 is used as a precursor, no significant changes in surface area occurred, but important changes in pore size distribution were detected. With Zr alkoxide, both the surface area and the porosity changed significantly. The catalytic activity for CH4 combustion depends mainly on the porosity of (1) and the presence of Ω, which induce an inhibitory effect on the combustion.
HOMOGENEOUS CATALYSIS

Copolymerization of Carbon Monoxide with Ethene Catalyzed by Bis-Chelated Palladium(II) Complexes Containing Diphosphine and Dinitrogen Ligands


[Pd(P-P)(N-N),]PF6 (P-P = 1,3-bis(diphenylphosphino)propane, meso-2,4-bis(diphenylphosphino)pentane (meso-bdpp), rac-2,4-bis(diphenylphosphino)pentane, 2,2'-bis(diphenylphosphino)ethylpentane; N-N = 2,2'-bipyridine (bipy; x = 1), 1,8-naphthyridine (x = 2)) were tested as catalyst precursors for the copolymerisation of CO and C2H4 in MeOH in either autoclaves or high pressure sapphire NMR tubes. [Pd(meso-bdp) (N,N'-bipy)]- (PF6)2 with both 1,4-benzoquinone and p-toluenesulfonic acid showed the best catalytic performance.

Catalytic Hydrogenation and Deuteration of Phospholipid Model Membranes with a Water-Soluble Rhodium(I) Complex Catalyst


The title Rh complex was an active catalyst for the hydrogenation of phospholipid liposomes in H2O under mild conditions. The highest conversion was achieved at pH 4.70. Formation of asymmetrically deuterated lipids, together with isomerisation and kinetic results demonstrated the important role of the reversible formation of an alkyl-Rh intermediate in the mechanism.

The First Efficient Hydroammonomethylation with Ammonia: With Dual Metal Catalysts and Two-Phase Catalysis to Primary Amines


The highly selective hydroammonomethylation of olefins with NH3 to form linear primary and secondary aliphatic amines with a new Rh/Ir/TPPTS catalyst (1) has been demonstrated. Aminomethylation of 1-pentene with synthesis gas (CO:H2 = 1:5) in the presence of (1) under standard hydroformylation conditions (130°C; 120 bar) in an aqueous two-phase system gave amines in 75% yield.

Highly Regio- and Enantio-Selective Rhodium-Catalysed Asymmetric Hydroformylation without Organic Solvents


The use of a Rh catalyst with a new perfluoroalkyl-substituted (R,S)-H7F2-2,7-BINAPHOS ligand (1) has allowed the efficient and highly regio- and enantioselective hydroformylation of vinyl arenes in compressed CO. Similar catalytic activity and the same level of enantiocontrol as (R,S)-2,7-BINAPHOS ligand in benzene, an ecologically and toxicologically hazardous organic solvent, are achieved. The substitution pattern of (1) is crucial for the unprecedented high regioselectivity.

Asymmetric Hydroformylation of Vinyl Acetate with BINAP-Rhodium(I) Complexes


(R)-BINAP-Rh(I) complexes derived from Rh(acac)-(CO)2 and [Rh(CO)(OMe)(cod)] were used for the asymmetric hydroformylation of vinyl acetate. Enantiomeric excesses of ≥60% were achieved with regioselectivities of ≤99%. Applying 10 bar of a 1:1 mixture of CO:H2 gave good activities and selectivities. The reaction rate is inversely dependent on the CO partial pressure. Increasing the H2 partial pressure leads to hydrogenation of the substrate.

Catalytic Water Oxidation Using Chemically Generated Ru(bpy)3+ Oxidant


In a catalytic O2 oxidation system composed of Ru[bpy]3+ and RuO2 adsorbing Ru-red, a much higher amount of O2 evolved than in a homogeneous Ru(bpy)3+/Ru-red system. The amount of O2 evolved increased with the amount of Ru-red adsorbed in RuO2, but higher amounts of absorbed Ru-red resulted in a decrease in O2 evolution. This is ascribed to bimolecular decomposition of Ru-red in the RuO2 at higher concentrations.

FUEL CELLS

Temperature and Pressure Dependence of O2 Reduction at Pt|Nafion® 117 and Pt|BAM® 407 Interfaces


Kinetically and mass transport parameters have been determined for the O2 reduction reaction at the interface between a Pt disk electrode (50 μm) and two solid polymer electrode membranes: Nafion® 117 (1) and a BAM® 407 membrane (2) (for PEMFC). These materials were investigated at 303-343 K and O2 pressures of 2-5 atm absolute, at 100% relative humidity. The membranes have similar permeabilities, but the diffusion coefficients and solubilities of O2 are very different, being related to the H2O content of the respective material.

ELECTRICAL AND ELECTRONIC ENGINEERING

Optimizing Pd-Ge Ohmic Contact to GaAs Through Microstructure Control

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DSC together with TEM was used to study the microstructure evolution and the corresponding solid state reactions that take place during the formation of Pd-Ge ohmic contacts on GaAs. Four solid state reactions were identified: Pd-Ge interdiffusion, hexagonal Pd,Ge formation, transformation into PdGe and excess Ge crystallisation. For good ohmic contact, Ge transport to the interface with GaAs is the key.