ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Theoretical Investigation of Isomer Stability in Platinum—Palladium Nanoalloy Clusters

The interatomic interactions of Pt–Pd nanoalloy clusters (1) were modelled by the Guptan many-body potential. For 18–20 atom clusters, a general algorithm was used to establish the lowest energy structures for each size and for all possible compositions. In the lowest energy isomers (homotemplates), the Pd atoms are mainly at the surface, with the Pt atoms preferentially occupying interior sites.

Dendrimer-Templated Ag–Pd Bimetallic Nanoparticles

Ultrafine amine-terminated fourth-generation starburst poly(amineamine) dendrimer-templated Ag–Pd bimetallic nanoparticles (1) were prepared from silver(I)-bis(oxalato)palladate(II) (2). The use of (2), in which two metal ions exist in one complex, prevented Ag halide formation. The particle size distributions of (1) were all in the narrow range of 2–5 nm, but were dependent upon the Ag/Pd ratio.

CHEMICAL COMPOUNDS

The Construction of P-O/P-N Ligands on Platinum and Palladium

PtIII and PdIII diphenylphosphinidene were prepared by adding diols to a solution containing cis-[MCl2(PPh2Cl)] (M = Pt or Pd) preformed in situ from cis-[MCl2(1,5-COD)] and PPh2Cl. As for the P-O bond, the P-N bond can be formed via nucleophilic attack of an amine group on coordinated PPh2Cl in the presence of base to give aminophosphine-phosphinite and N,N'-bis(antipyril-4-methyl)-piperazine complexes of PtIII and PdIII.

C–H and N–H Activation by Pt(0) in N- and O-Heteroaromatic Compounds

Pt[Pt(PPh3)4] reacts with azoles to give Pt(II) hydride complexes, trans-[PtH(1-azolyl)(PPh3)2] (azolyl = indolyl, imidazolyl, benzimidazolyl, pyrazolyl, indazolyl), by oxidative insertion of the Pt centre into the N–H bond of the respective azoles. Pyrrole was much less reactive. The trans-[PtH[R](PPh3)2] complexes (R = 2-furyl, 2-benzoxazolyl, 2-benzothiazolyl) were prepared via C–H bond activation.

ELECTROCHEMISTRY

The Electrochemical Formation and Properties of Bilayers Composed of Polypyrrole and C60Pd Films

Bilayers of polypyrrole and C60Pd were prepared by sequential electropolymerisation of the parent monomers and investigated by cyclic voltammetry. For the electrode/polypyrrole/C60Pd bilayer, the high permeability of the C60Pd film for the supporting electrolyte ions allowed the oxidation of the polypyrole inner layer. For the electrode/C60Pd/polypyrrole bilayer, the outer polypyrrole layer inhibited the reduction of the inner C60Pd layer.

PHOTOCONVERSION

Effects of Chlorine Gas Exposure on the Optical Properties of Rhodium Phthalocyanine Films

Rh phthalocyanine films (1) were deposited on glass by the Langmuir-Blodgett technique. On exposure to Cl2 (1) changed from blue to transparent. Incorporation of Cl2 caused quenching of the characteristic triplet centred around the Q-absorption band at 662 nm. Leaving prior Cl2 exposed (1) in air for several hours resulted in a slow partial recovery of the optical spectra.

A Synthesis and Luminescence Study of Ir(ppy)3 for Organic Light-Emitting Devices

OLEDs were fabricated with doped films of tris(1-phenyl-κC1-pyrazolato-κN2)iridium (1) in several hosts. The electroluminescence peak occurred at 450 nm. The luminance of the OLEDs was pure blue, but luminous efficiencies were low since the LUMO of (1) was higher than those of the hosts.

Photobleaching and Single Molecule Detection of a Phosphorescent Organometallic Iridium(III) Complex

The photostability of bulk samples of Ir(ppy)3 (1) (ppy = 2-phenylpyridine) in polymer films was examined by measuring the photobleaching kinetics under intense laser irradiation. On a single molecule level, (1) was characterised by phosphorescence time traces, distribution of phosphorescence intensity levels and by polarisation modulated excitation.
Synthesis and Characterization of Naphthyridine and Acridinedione Ligands Coordinated Ruthenium(II) Complexes and Their Applications in Dye-Sensitized Solar Cells


The title complexes were synthesised and characterised, and then used in dye-sensitised solar cells. From the I–V curves, the short-circuit photocurrent (Isc) and the open-circuit photovoltage (Voc) were measured. A maximum current conversion efficiency of ~ 7.7% was achieved by the 5-amino-4-phenyl-2-(4-methylphenyl)-7-(pyrrolidin-1-yl)-1,6-naphthyridine-8-carbonitrile coordinated Ru(II) complex.

ELECTRODEPOSITION AND SURFACE COATINGS

Mesoporous Microspheres Composed of PtRu Alloy


Electrochemical co-reduction of H2PtCl6 and RuCl3 dissolved in the aqueous domains of the liquid crystalline phase of an oligoethoxylene oxide surfactant (C20EO8) gave the title microspheres (1) (0.5–1 μm). The ordered mesoporous internal structure of (1) involves periodic pores of ~ 2.4 nm in diameter separated by walls of ~ 2.4 nm thick. (1) have high specific surface area.

Synthesis of PtN2 Films by Reactive Laser Ablation


Thin films of Pt (1) with ~ 14 at.% N were prepared by reactive laser ablation in molecular N2 ambient. AES, XPS and electron energy loss spectroscopy were used to characterise (1). The existence of chemisorbed N was supported by the N1s binding energy of 398.4 eV. The +0.2 eV shift of the Pt 4f peak position indicated charge transfer from Pt to N. The Pt formed an incipient nitride phase with composition near to Pt6N.

APPARATUS AND TECHNIQUE

Calorimetric Hydrocarbon Sensor for Automotive Exhaust Applications


The sensor (1) is a thermoelectric device supported on a planar Al2O3 substrate. A non-selective Pt catalyst was used in (1) to detect hydrocarbons with high selectivity. For CO detection (1) uses a CO oxidation catalyst of Pb-modified Pt, which exhibits excellent CO selectivity at 200–400°C. (1) gave a linear output of 0–2.75 mV over 0–1000 ppm of propylene (at 350°C). Engine dynamometer evaluation showed that the response of (1) paralleled the change in concentration of the CO and hydrocarbons when the engine air/fuel ratio was varied.

Chemiresistor Coatings from Pt- and Au-Nanoparticle/Nonanethiodiol Films: Sensitivity to Gases and Solvent Vapors


Layer-by-layer self-assembly using 1,9-nonanediol and dodecylamine-stabilised nanoparticles of Pt or Au gave films (1) of thickness, 66 ± 2 and 31 ± 1 nm, respectively. The sensitivity of (1) was investigated by dosing them with NH3, CO and vapours of H2O and toluene (300 ppb–5000 ppm). (1) have a high signal/noise ratio. A detection limit for NH3 < 100 ppb was achieved. NH3 and CO bind to vacant sites on the metal nanoparticle cores.

HETEROGENEOUS CATALYSIS

Palladium(II) Chloride Catalyzed Selective Acetylation of Alcohols with Vinyl Acetate


PdCl2 with CuCl2 can be used for the catalytic acetylation of primary and secondary alcohols with vinyl acetate. The reaction is carried out in dry toluene at room temperature. The catalyst system can be recovered by filtration. The acetaldehyde byproduct can be removed by evaporation along with the toluene solvent. This mild reaction proceeds more rapidly with primary alcohols.

Assembled Catalyst of Palladium and Non-Cross-Linked Amphiphilic Polymer Ligand for the Efficient Heterogeneous Heck Reaction


An insoluble catalyst (1) was prepared from self-assembly of (NH4)2PdCl4 and a non-cross-linked amphiphilic phosphate polymer. (1) in only 5.0 × 10–5 mol equiv. concentration was effective for the heterogeneous Heck reaction of aryl iodides with acrylates, styrenes and acrylic acid. (1) could be recycled five times. (1) showed good stability in toluene and H2O and so efficiently catalysed the Heck reaction in these media. (1) can be used for the synthesis of resveratrol, a cyclooxygenase-II inhibitor.

Effect of Activated Carbon and Its Surface Property on the Activity of Ru/AC Catalyst


Activated C was pretreated by washing with HNO3 and then calcined before the preparation of Ru/activated C catalysts (1) for NH3 synthesis. The HNO3 treatment increased the catalytic activity from 17.4 to 19%, respectively. The Ru dispersion and catalytic activity were improved from 43 to 62% and 17.4 to 19%, respectively.
HOMOGENEOUS CATALYSIS

The First Platinum-Catalyzed Hydroamination of Ethylene

The hydroamination of ethylene with anilines, using PdBr2 as a catalyst precursor in n-Bu4PBr under 25 bar of ethylene pressure, gave N-ethylaniline with 80 turnovers after 10 h at 150°C. 2-Methylanilines were simultaneously produced in ~10 cycles. Additions of P(OMe)3 (2 equiv./PdBr2) or of a proton source (3 equiv./PdBr2) were beneficial. A TON of 145 after 10 h at 150°C was achieved with a biphasic system (n-Bu4PBr/decanol) in the presence of CH3NH3+. The lower the basicity of the amine, the higher the TON.

Important Consequences for Gas Chromatographic Analysis of the Sonogashira Cross-Coupling Reaction

Typical quenching procedures for GC analysis of the Sonogashira reaction for 4-bromo-6-methyl-2-pyrone with phenylacetylene (catalysed by (Ph3P)2PdCl2) cannot be used. Turnover continues to occur in sample vials even after quenching by commonly used SiO2 adsorption and product elution with CH2Cl2. Trace amounts of Pd are carried through the SiO2 plug. Addition of 1,2-bis(diphenylphosphino)ethane to the sample inhibited any further reaction.

Role of Base in Palladium-Catalyzed Arylation of Carbanions

The arylation of carbanions, derived from various sulfones, cyanoacetic ester and malononitrile, with aryl bromides using Pd2dba3/3L, L = PPh3, P sulfones, cyanoacetic ester and malononitrile, with 4-CF3C6H4 Pd(PPh3)2Br were carried out. A base (n-Bu4PBr) was a prerequisite for high enantioselectivity. The stronger (16–20%). A free hydroxyl group on the ligand was a prerequisite for high enantioselectivity. The stronger the base present, the higher the conversion.

NEW CHIRAL BIS(OXAZOLINE) RH(III)-, IR(III)- AND RU(II)-COMPLEXES FOR ASYMMETRIC TRANSFER HYDROGENATIONS OF KETONES

The transfer hydrogenation of acetoephene in 2-propanol was used to examine the title complexes. The Ru(II)-based catalyst exhibited good activity with 50% conversion and high enantioselectivity (89%), whereas the Rh(III)- and Ir(III)-complexes gave low conversions (~20%) and poor enantioselectivities (16–20%). A free hydroxyl group on the ligand was a prerequisite for high enantioselectivity. The stronger the base present, the higher the conversion.

FUEL CELLS

Effect of Preparation Conditions of Pt/C Catalysts on Oxygen Electrode Performance in Proton Exchange Membrane Fuel Cells
Pt/C catalysts with 3.2 nm Pt crystallites were prepared by the impregnation-reduction method, varying conditions such as the reaction temperature, the concentration of H2PtCl6 and different reducing agents. Heat treatment in N2 of the C black support improved Pt dispersion and increased the relative content of Pt (111) orientation. This benefited the acceleration of the oxygen reduction reaction in the PEMFC.

Preparation and Performance of Pt-Co/C Catalyst for PEMFC
Pt-Co/C electrocatalysts (1) were prepared by the liquid deposition and high temperature alloying method. The Pt and Pt-Co have f.c.c. structure, with small particle size and high dispersity. The Co addition shortened the length of the Pt–Pt bond. (1) showed better performance than Pt/C in PEMFCs. The Co addition exhibited high catalytic activity.

ELECTRICAL AND ELECTRONIC ENGINEERING

Microstructure and Magnetic Properties of Bamboo-Like CoPt/Pt Multilayered Nanowire Arrays

Double-pulse electrodeposition into the pores of a porous anodic Al oxide template gave highly ordered CoPt/Pt multilayered nanowire arrays (1). The nanowires had a bamboo-like structure. The section lengths could be adjusted by varying the pulse width and pulse intensity. (1) exhibited in-plane anisotropy. High coercivity (Hc = 1.8 kOe) and squareness (Mr/Ms) ~ 0.35 were obtained in (1) when the field was applied perpendicular to the wire axis of (1). This is attributed to the disordered f.c.c. CoPt formation.

Effects of Post-Annealing on the Dielectric Properties of Au/BaTiO3/Pt Thin Film Capacitors
BaTiO3 thin films (1) were prepared by the polymeric precursor method and deposited onto Pt/Ti/SiO2/Si. The BaTiO3 perovskite phase formation was investigated. (1) were post-annealed in O2 and N2 at 300°C for 2 h. Post-annealing in O2 increased the dielectric relaxation phenomenon, whereas in N2 a slight dielectric relaxation was produced.