ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Microstructure and Shape Memory Behavior of Tl₄₋₀.₅(Pd₁₋₀.₅Ni₁₋₀.₅) and Tl₉₋₀.₅(Pd₂₋₀.₅Ni₂₋₀.₅) Thin Films

Ti-rich (Tl₂₋₀.₅(Pd₁₋₀.₅Ni₁₋₀.₅)) and near-equiatomic (Tl₉₋₀.₅(Pd₂₋₀.₅Ni₂₋₀.₅)) thin films were annealed at 773, 873 and 973 K from the amorphous state. At < 973 K, these crystallisations are effective for grain refinement. Film (1), annealed at 773 K, has fine plate-like Ti₃Pd-type precipitates with a diameter < 100 nm inside the B2 grain. The shape memory characteristics can be improved by precipitate hardening.

Hydrogen Absorption of Nanoscale Pd Particles Embedded in ZrO₂ Matrix Prepared from Zr–Pd

Nanoscale Pd particles in an isolated dispersed state embedded in ZrO₂ matrix gave maximum H₂ absorption amounts of ~ 2.4 mass% (H₂/Pd) at 323 K and 2.2 mass% (H₂/Pd) at 423 K with H₂ pressure of 1 MPa. In contrast, Pd metal in bulk and powder forms gave only 0.7 and 1.2 mass%, respectively.

CHEMICAL COMPOUNDS

Multinuclear Magnetic Resonance Studies of the Aqueous Products of the Complexes cis- and trans-Pt(Ypy)₂(NO₃)₂ Where Ypy = Pyridine Derivative

The product of the cis title complexes undergoing aquation in acidic pD was cis-[Pt(Ypy)₂(D₂O)]²⁺, whereas hydrolysis in basic medium gave cis-[Pt(Ypy)₂(OH)]²⁻. Complexes containing 2-picoline and 2,4-lutidine ligands behaved differently in their ¹⁹⁵Pt NMR due to the ortho effect. The trans analogues showed two signals in acidic pD corresponding to the diaqua monomer and the monohydroxo-bridged aqua dimer. Two species were also observed in basic pD.

Nonradical Trapping Pathway for Reactions of Nitroxides with Rhodium Porphyrin Alkyls Bearing β-Hydrogens and Subsequent Carbon–Carbon Bond Activation

A novel nitroxide-induced H atom abstraction and β-elimination of Rh porphyrin alkyls was demonstrated. Subsequent C-C bond activation of methyl-substituted nitroxides by the Rh(II) porphyrin radical yielded Rh(II) porphyrin methyl complexes.

Liquid-Crystalline Materials Based on Rhodium Carboxylate Coordination Polymers: Synthesis, Characterization and Mesomorphic Properties of Tetra(alkoxybenzoato)dirhodium(II) Complexes and Their Pyrazine Adducts

Rh₂(x,y-x-BmOCo)₄ (β = benzoate group; m = number of alkoxy chains on the aromatic ring; x, y, τ = their anchoring positions; n = number of C atoms in each alkoxy chain) and their pyrazine adducts (with polymeric structure via connected metallo centres) were synthesised. Most exhibit LC columnar and cubic mesophases with melting transition temperatures close to or below room temperature. The equatorial ligands of the adducts fill the interdimeric space.

Piano-Stool Inversion in Arene Complexes of Ru(II): Modelling the Transition State

[RuH(arene)(Binap)]CF₃SO₃ (arene = η⁵-benzene (1) or η⁶-toluene) was prepared. The structures were markedly distorted from a classical three-legged piano-stool structure with (1) having the P–Ru–P plane ~ perpendicular to the plane of the arene. The structure of (1) indicates a transition state leading from one diastereomer to another via inversion at Ru.

ELECTROCHEMISTRY

Degradation Mechanism of Long Service Life Ti/IrO₂-Ta₂O₅ Oxide Anodes in Sulphuric Acid

Ageing studies of Ti/70% IrO₂-30% Ta₂O₅ anodes over the whole of their electrolysis time in H₂SO₄ established that their performance can be divided into ‘active’, ‘stable’ and ‘deactive’ regions. In the first two stages, the loss of coated oxides is dominated by dissolution of the active component (IrO₂ exhibits preferential loss). In the ‘deactive’ region, the oxide coatings are lost mainly by peeling at the Ti/oxide layer interface region.

Preparation and Electrochemical Characterization of Ti/Ru,Mn₂₋₅,O₂ Electrodes

DSA® type electrodes of Ru–Mn mixed oxides (30 ≤ at.% Ru < 100) supported on Ti were prepared by spray pyrolysis. Polarisation curves were used to evaluate their behaviour as anodes for the Cl₂ and O₂ evolution reactions. A composition of ~ 70 at.% Ru gave the best electrocatalytic activity and stability.
PHOTOCONVERSION

The Singlet-Triplet Energy Gap in Organic and Pt-Containing Phenylene Ethynylene Polymers and Monomers

The evolution of the Ti triplet excited state in a series of phenylene ethynylene polymers (1) and monomers with Pt atoms in the polymer backbone and in an analogous series of all-organic polymers (2) with the Pt(II) tributylphosphonium complex being replaced by phenylene was studied. The Pt increases spin-orbit coupling so the Ti state emission (phosphorescence) is easier to detect. For both (1) and (2), the Ti state was at a constant separation of 0.7 ± 0.1 eV below the singlet Si state.

The Effect of pH on the Emission and Absorption Spectra of a Ruthenium Complex

The protonable ligand for the Ru(1,10-phenanthroline)2,(3-carboxylate,4-hydroxy-1,10-phenanthroline)24- (PPh3) complex (1) is readily prepared. (1) has a small spectrophotometric change that results in a large emission intensity change. The emission intensity of (1) is pH dependent in the pH range 3–11. (1) is useful for luminescence-based pH sensors.

ELECTRODEPOSITION AND SURFACE COATINGS

Crystallographic and Electrical Properties of Platinum Film Grown by Chemical Vapor Deposition Using (Methylcyclopentadienyl)trimethylplatinum

Pt thin films (1) grown by CVD using MeCpPtMe3 were found to contain O and C impurities. The C impurities produce a microgran morphology that contributes to high residual resistivity. High O contamination is observed, irrespective of the O2/Ar ratio during growth. The intrinsic electrical transport property is not affected by the contaminants. (1) grown under oxidative conditions have good electrical properties so are useful as electrodes for MIM capacitors.

Electrodeposition of Osmium
T. JONES, Met. Finish., 2002, 100, (6), 84, 86–90

The electrodeposition of Os is reviewed. The alkaline process, hexachloro-osmate process, nitrosyl complex process and molten salt process are described. Blackening of the Os deposit for the hexachloro-osmate process is prevented by the use of dual anodes inside and outside a large porous pot. Very limited data on the deposit properties are available. Details of applications, alloys, analytical control techniques and toxicity are included. (19 Refs.)

APPARATUS AND TECHNIQUE

Polysilicon Mesoscopic Wires Coated by Pd as High Sensitivity H2 Sensors

Mesoscopic poly-Si wires coated by a thin film of Pd (100 nm) can be used as H2 sensors. Using surface micromachining combined with a usual microelectronic planar process, poly-Si wires of the following dimensions were fabricated: 0.25–3.7 μm wide, 100–140 μm long, and ~ 600 nm thick. Because of their high surface/volume ratio, these wires exhibit a very high resistance percentage variation under H2 absorption.

CH4 Decomposition with a Pd–Ag Hydrogen-Permeating Membrane Reactor for Hydrogen Production at Decreased Temperature

The CH4 decomposition reaction into C and H2 over Ni/SiO2 was investigated using a Pd–Ag H2-permeating membrane reactor. Removing the formed H2 with the Pd–Ag membrane increases the CH4 decomposition activity (> 88%) at < 773 K. A higher H2 permeation rate was achieved with 77Pd-23Ag than with 90Pd-10Ag, thus increasing CH4 conversion. The H2 formed was > 99.99% pure.

HETEROGENEOUS CATALYSIS

Deep Oxidation of VOC Mixtures with Platinum Supported on Al2O3/Al Monoliths

Pt impregnated metallic monoliths (1) were prepared from anodised Al foils. The catalytic oxidation activity of (1) was tested for the VOCs: 2-propanol, toluene, methyl ethyl ketone, acetone and their mixtures. Complete oxidation was achieved except for 2-propanol, where acetone was found as an oxidation intermediate. Even if the adsorption of the VOC on the Al2O3 is governed by its polarity, the reactivity is mainly affected by the competition of the O atoms chemisorbed on the Pt particles.

Isomerization and Hydrocracking of n-Decane over Bimetallic Pt–Pd Clusters Supported on Mesoporous MCM-41 Catalysts

Pt-Pd/AlMCM-41 (1) is superior to Pt/AlMCM-41 and Pd/AlMCM-41 for n-decane isomerisation. The use of (1) results in a higher C10 isomer yield at a substantially lower reaction temperature. (1) has a better balance between the two catalytic functions, namely acid sites and metal sites.
Laser-Activated Membrane Introduction Mass Spectrometry for High-Throughput Evaluation of Bulk Heterogeneous Catalysts

E. A. LAMIMS has been used to evaluate catalysts such as Pt/Ce02-ZrOz under realistic conditions. The catalyst array is supported on C paper overlaid upon a silicone rubber membrane configuration in a variation of MIMS. The C paper serves as a heat-dissipating gas diffusion layer that allows laser heating of catalyst samples to far above the decomposition temperature of the polymer membrane that separates the array from the mass spectrometer vacuum chamber. A bulk catalyst array spot can be evaluated for activity and selectivity in as little as 90 seconds.

Catalytic Activity and Poisoning of Specific Sites on Supported Metal Nanoparticles


Molecular beam methods and time-resolved reflection-absorption IR spectroscopy were combined in order to investigate MeOH decomposition on Pd nanoparticles/AI2O3/NiAl(110) model catalyst. Two competing reaction pathways were observed: a rapid dehydrogenation to give CO and a slow C-O bond breakage to form C and hydrocarbon species. It was shown that C-O bond breakage occurs preferentially at particle step and edge sites.

Hydrogenation of Phenol by the Pd/Mg and Pd/Fe Bimetallic Systems under Mild Reaction Conditions


Three Pd-catalysed zerovalent metal systems were able to hydrogenate phenol to cyclohexanol and cyclohexanone at room temperature and pressure. Treatment of aqueous phenol solutions (5.0 mM) with Pd (2.6 ppt m/m)/Mg (1.00 g 20 mesh) and with 0.53 g of 1/8 in. Pd (0.5%/Al2O3 in contact with 1.00 g 20 mesh Mg resulted in 74% and 24% destruction, respectively, of the reactant after 6 h. The Pd/Al2O3 with Mg system was greatly enhanced by 2% v/v glacial acetic acid, resulting in an 84% reduction of phenol with a C balance of 93%.

Self-Regeneration of a Pd-Perovskite Catalyst for Automotive Emissions Control


X-Ray diffraction and absorption established that LaFe0.75Co0.25Pd0.05O3 autocatalyst (1) retains high metal dispersion owing to structural responses to the fluctuations in exhaust gas composition. As (1) is cycled between oxidative and reductive atmospheres, Pd reversibly moves into and out of the perovskite lattice.

HOMOGENEOUS CATALYSIS

High-Throughput Screening Studies of Fiber-Supported Catalysts Leading to Room-Temperature Suzuki Coupling

T. J. COLACOT, E. S. GORE and A. KUBER, Organometallics, 2002, 21, (16), 3301-3304

High-throughput screening of Ph3P-based polymer-supported catalysts such as FibreCat™-1001 and selected Pd/C catalysts gave nearly quantitative conversion of activated and unactivated aryl bromides in Suzuki coupling using EtOH/H2O. The FibreCat catalysts did not leach Pd. For p-chloroacetophenone and 3-bromothiophene, coupling could be possible by tuning the FibreCat catalysts with t-Bu3P.

 Palladium Catalyzed Oxidation of Monoterpenes: Novel Oxidation of Myrcene with Dioxygen


Myrcene (7-methyl-3-methylene-1,6-octadiene) can be efficiently and selectively oxidised by O2 in glacial acetic acid containing LiCl, with PdCl2, CuCl2. New monoterpenes with a cyclopentane skeleton, 3- and 4-(1-acetoxy-1-methylethyl)-1-vinylcyclopentene, were produced. These products have a pleasant scent with a flower or fruit tinge and have potential as components of synthetic perfumes.

Novel Synthesis of Fused Isoxazolidines via a Palladium Catalysed Allene Insertion–Intramolecular 1,3-Dipolar Cycloaddition Cascade Reaction


 Aryl iodides react with allene (1 atm) and nitrore in toluene at 120°C over 48 h in the presence of 10 mol% Pd(OAc)2, 20 mol% PPh3 and Cs2CO3 to afford the corresponding isoaxazolidines in 50–77% yield. The synthesis is a one pot reaction involving a Pd catalysed allenation of the aryl iodide in combination with a nitrore cycladdition, creating two rings, two stereocentres and one tetrasubstituted C centre.

Polymerization of Phenylacetylene Catalyzed by Diphosphinopalladium(II) Complexes


Cationic bis(phosphino)Pd complexes were generated in situ by the reaction of (dppf)PdCl(CH3), (dippf)PdCl(CH3), (dppf)PdCl, (dippf)PdCl, and (dppf)PdCl (dppf = bis(diphenylphosphino)ferroene, dippf = bis(diisopropylphosphino)ferroene and dppf = bis(diphenylphosphino)ethane) with AgOTf. The dppf- and dippf-Pd complexes catalysed the polymerisation of phenylacetylene, whereas the dppf analogues formed phenylacetylene oligomers. The highest molecular weight polymer was obtained from a 1:1 CH2Cl2/CH3CN mixture at room temperature. This seemed to be the best conditions for polymerisation.
A Simple, Recyclable, Polymer-Supported Palladium Catalyst for Suzuki Coupling – An Effective Way to Minimize Palladium Contamination


Preparation of a polymer-supported catalyst (1) involved wet impregnation of a polymer-bound phosphine with PdCl2 in EtOH. (1) was used for Suzuki coupling. After each cycle (1) was recyclable with low Pd leaching. The Suzuki coupling of an arylbromide with P-trifluoromethylphenylboronic acid resulted in the synthesis of 2-amino tetralin, used in the treatment of epilepsy, stroke, and brain or spinal trauma.

1,3-Dipolar Cycloaddition Reactions of Carbonyl Ylides with 1,2-Diones: Synthesis of Novel Spiro Oxabicycles


A facile 1,3-dipolar cycloaddition reaction of carbonyl ylides with a range of o-quinones afforded highly oxygenated spiro oxabicycles. Rh2(OAc)3 was employed as the catalyst. The reactions were carried out in toluene at room temperature under an atmosphere of Ar. For 1,2-benzoquinones, the ylide preferentially adds to the more electron deficient of the two carbonyls of the quinone.

A Free Ligand for the Asymmetric Dihydroxylation of Olefins Utilizing One-Phase Catalysis and Two-Phase Separation


A free bis-cinchona alkaloid derivative (1) was used as the ligand in the Os-catalysed asymmetric dihydroxylation of olefins. (1) can be easily prepared. The molar ratio of (1)/olefin was 5%, which was much lower than that required for the corresponding soluble polymer-supported cinchona alkaloid ligands (10–25%). Yields of 89–93% and ee of 89–99% were achieved with (1). Repetitive use of (1) is possible without significant loss of enantioselectivity when a small quantity of OsO4 is added after each run.

The Oxidation of Alcohols in Substituted Imidazolium Ionic Liquids Using Ruthenium Catalysts


Substituted imidazolium ionic liquids may be used as solvents for the oxidation of alcohols to aldehydes and ketones using [Pr3N][RuO4] (1) as the source of the metal catalyst. (1) was used in conjunction with either N-methylmorpholine-N-oxide or O2 as cooxidants. Benzylic alcohols were oxidised to their aldehydes in good to excellent yields, whereas aliphatic alcohols required much longer reaction times and gave poor yields.

FUEL CELLS

Fundamental Aspects in Electrocatalysis: from the Reactivity of Single-Crystals to Fuel Cell Electrocatalysts


Nanostructured Pt-Ru electrodes prepared by metal electrodeposition exhibited distinct characteristics regarding CO oxidation due to a cooperative reaction mechanism involving CO surface mobility. For Pt-Ru/C catalyst, prepared by the sulfito method, at 25°C the mass activity increases with increasing catalyst mass loading \( \leq 55 \text{ wt.\%} \). Then a plateau in the mass activity vs. weight loading is reached. At 65°C, a maximum mass activity occurs at 60 wt.%. A Free Ligand for the Asymmetric Dihydroxylation of Olefins Utilizing One-Phase Catalysis and Two-Phase Separation

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