

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Grain Growth in Ultrathin Films of CoPt and FePt

R. A. RISTAU, K. BARMAK, K. R. COFFEY and J. K. HOWARD, *J. Mater. Res.*, 1999, **14**, (8), 3263–3270

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-Cr₂C₂ Alloys at 1, 100 and 1,200°C

F. H. STOTT, B. GLEESON and P. CASTELLO, *Mater. High Temp.*, 1999, **16**, (1), 15–26

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

M. TABIB-AZAR and B. SUTAPUN, *Rev. Sci. Instrum.*, 1999, **70**, (9), 3707–3713

Evanescent 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 × 10⁷ 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 0.01–4% could be detected by the EMP.

Magnetic Properties of RPd₃S₄ (R = Ce, Gd)

M. WAKESHIMA and Y. HINATSU, *J. Solid State Chem.*, 1999, **146**, (1), 226–229

GdPd₃S₄ shows antiferromagnetic behaviour below 5.8 K. Above 10 K, the magnetic susceptibility follows the Curie law, and the effective magnetic moment is 7.36 μ_B. CePd₃S₄ shows ferromagnetism below 5.8 K. The residual magnetisation is 0.39 μ_B and the magnetic moment at 5 T is 0.83 μ_B at 2 K. From the magnetic transition temperature of RPd₃S₄, the superexchange interaction is thought to be dominant in the magnetic interaction.

Alloying Elements Partitioning in TiAl-Ru Intermetallic Alloys

S. KIM, D. J. LARSON and G. D. W. SMITH, *Intermetallics*, 1999, **7**, (11), 1283–1290

The solute partitioning behaviour in two phase α₂ + γ Ti-48 at.% Al-0.5 at.% Ru alloys was investigated using atom-probe field-ion microscopy. Ru was depleted in α₂ and interstitial elements were localised in the α₂ phase. The degree of localisation for interstitials is much more significant than for substitutional elements.

Infrared Spectra and Density Functional Calculations of RuCO⁺, OsCO⁺, Ru(CO)_x⁻, Os(CO)_x⁻, Ru(CO)_x⁻ and Os(CO)_x⁻ (x = 1–4) in Solid Neon

M. ZHOU and L. ANDREWS, *J. Phys. Chem. A*, 1999, **103**, (35), 6956–6968

Laser ablated Ru and Os atoms were co-deposited with CO (0.05–0.2%) during condensation in excess Ne. M(CO)_x (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 [Pt₂Cu₄(C≡CPh)₆]₂

V. W.-W. YAM, K.-L. YU and K.-K. CHEUNG, *J. Chem. Soc., Dalton Trans.*, 1999, (17), 2913–2915

[Pt₂Cu₄(C≡CPh)₆]₂ (1) was synthesised by the reaction of [NBu₄]₂[Pt(C≡CPh)₄] (2) with [Cu(MeCN)₄][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 ν(C≡C) absorption to a lower wavenumber in (1) than in (2) was indicative of a π-bonding mode of the alkynyl ligands.

Palladium and Platinum Dithiocarbamate Complexes Containing Mono- and Diamines

V. SCARCIA, A. FURLANI, D. FREGONA, G. FARAGLIA and S. SITRAN, *Polyhedron*, 1999, **18**, (22), 2827–2837

[M(DMDT)X]_n (M = Pd, Pt; DMDT = Me₂NCS₂; X = Cl, Br) were reacted with amines (Am) (Py, pyridine; Pra, n-propylamine; Cba, cyclobutylamine; Dap, 1,3-diaminopropane; En, ethylenediamine) to give M(DMDT)(L)₂X (L = Py, Pra, Cba), [M(DMDT)(L₂)X], [M(DMDT)(En)]X and [M(DMDT)(Dap)]X. TGA data suggest a particular behaviour for Pd-Pra and Pd-Cba, with the formation of low stoichiometry intermediates Pd₂(DMDT)₂AmX₂.

Design of Novel Hexametallic Cartwheel Molecules from Persubstituted Benzene Compounds

H. P. DIJKSTRA, P. STEENWINKEL, D. M. GROVE, M. LUTZ, A. L. SPEK and G. VAN KOTEN, *Angew. Chem. Int. Ed.*, 1999, **38**, (15), 2186–2188

Nanosized hexametallic Pd^{II} species with persubstituted benzenes C₆[3,5-(CH₂Y)₂C₆H₃]₆ (Y = NMe₂, P(O)Ph₂, PPh₂, SPh) were synthesised. The molecular structure of [C₆{3,5-(CH₂SPh)₂C₆H₃(PdCl)}₆] showed C₃ symmetry with adjacent radial Pd–Pd separations of 7.339(2) and 8.006(2) Å and a diametrically opposed Pd–Pd separation of 15.340(2) Å. These cartwheel structures are potential homogeneous catalysts which can be recovered by nanomembrane filtration techniques.

Dicarbonylcyclopentadienyliridium, (η-C₅H₅)Ir(CO)₂, as a Ligand

F. JIANG, K. BIRADHA, W. K. LEONG, R. K. POMEROY and M. J. ZAWOROTKO, *Can. J. Chem.*, 1999, **77**, (8), 1327–1335

Using CpIr(CO)₂ as a 2e donor ligand, the metal complexes Cp(OC)₂IrW(CO)₅ (1), Cp(OC)₂IrRu(CO)₃(SiCl₃)₂, Cp(OC)₂IrOs(CO)₃(GeCl₃)(Cl) (2) and Cp(OC)₂IrOs(CO)₃(X)₂ (X = Cl, Br (3), I) 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)₅.

Synthesis and Characterization of a Metal Coordination Polymer Consisting of Ruthenium(III) β-Diketone Units Linked by Butadiyne Bridges

Y. HOSHINO and Y. HAGIHARA, *Inorg. Chim. Acta*, 1999, **292**, (1), 64–72

[Ru(mESima)]_n (mESima⁻ = 3-(trimethylsilyl)ethynyl-2,4-pentanedionate) and [Ru(mEma)]_n (mEma⁻ = 3-ethynyl-2,4-pentanedionate), were prepared as precursors for polymerisation to give the title Ru(III) polymer (1). The number-average molecular weight of (1), 5400, corresponding to ~ 11 monomer units, was obtained from the FT-NMR integrated intensities for the protons on the ethynyl group of the mEma ligand end-group relative to the CH₃-protons of the entire chain. NMR showed that (1) has a chain-like structure.

ELECTROCHEMISTRY

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

J. RAMBLA, E. BRILLAS and J. CASADO, *J. Appl. Electrochem.*, 1999, **29**, (10), 1211–1216

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.

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

C. LIN, J. A. RITTER and B. N. POPOV, *J. Electrochem. Soc.*, 1999, **146**, (9), 3155–3160

Sol-gel high surface area C-Ru xerogel composites (1) were prepared from carbonised resorcinol-formaldehyde resins containing RuO₂·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 RuO₂ were completely reversible.

PHOTOCONVERSION

Hydrogen Evolution Photoinduced by Using Platinum-Loaded Langmuir-Blodgett Films of Viologen-Linked Porphyrin

H. HOSONO, *J. Photochem. Photobiol. A: Chem.*, 1999, **126**, (1–3), 91–97

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

H. KUNKELY and A. VOGLER, *Chem. Phys. Lett.*, 1999, **308**, (3, 4), 169–172

Pd₃(acetate)₆ (1) shows photoluminescence in benzene at λ_{max} = 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 dσ* → pσ excited state, involving metal-metal interaction in the triangular (Pd^{II})₃ moiety.

Iridium(III) Bis-terpyridine Complexes Displaying Long-Lived pH Sensitive Luminescence

M. LICINI and J. A. G. WILLIAMS, *Chem. Commun.*, 1999, (19), 1943–1944

The title Ir(III) complexes in which the terpyridine ligands bear pendent protonatable (pyridyl) (1) or deprotonatable (phenolic) (2) groups have been prepared. Complexes with (1) display long-lived emission at pH 7 in air-equilibrated aqueous solution, but both the lifetime and intensity are reduced by a factor of > 8 upon protonation of the pyridyl nitrogen; the structurally similar complexes with (2) are only weakly emissive and their ground-state absorption spectra exhibit a new, low energy band (λ = 468 nm) upon deprotonation. These complexes constitute potential new pH sensory systems.

Luminescent Nafion Membranes Dyed with Ruthenium(II) Complexes as Sensing Materials for Dissolved Oxygen

D. GARCÍA-FRESNADILLO, M. D. MARAZUELA, M. C. MORENO-BONDI and G. ORELLANA, *Langmuir*, 1999, **15**, (19), 6451–6459

Indicator layers for luminescence optosensing of O₂, showing no dye leaching and avoiding the use of adsorbing materials, were developed by using [RuL₂]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]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]²⁺ in 178 μm thick Nafion.

ELECTRODEPOSITION AND SURFACE COATINGS

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

J.-Y. ZHANG and I. W. BOYD, *Solid State Electron.*, 1999, **43**, (6), 1107–1111

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

M.-C. JUNG, H.-D. KIM, M. HAN, W. JO and D. C. KIM, *Jpn. J. Appl. Phys.*, 1999, **38**, (8), 4872–4875

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

L.-M. ANG, T. S. A. HOR, G.-Q. XU, C.-H. TUNG, S. ZHAO and J. L. S. WANG, *Chem. Mater.*, 1999, **11**, (8), 2115–2118

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

M. A. EL KHAKANI, B. LE DROGOFF and M. CHAKER, *J. Mater. Res.*, 1999, **14**, (8), 3241–3246

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.

APPARATUS AND TECHNIQUE

The Use of Polymers Coupled with Metallised Electrodes to Allow H₂O₂ Detection in the Presence of Electrochemical Interferences

D. J. DALY, C. K. O'SULLIVAN and G. G. GUILBAULT, *Talanta*, 1999, **49**, (3), 667–678

The co-deposition of Ru, Rh and Pt as well as Pt on Ru-Rh electrodes was investigated to provide an electrode surface which is highly catalytic and selective towards H₂O₂. All transducers were coupled with polymers for enhanced response, due to elimination of interferences. A Ru-Rh metallised electrode polymerised with poly(1,3-diaminobenzene) gave the best results. At an applied potential of +100 mV the response to H₂O₂ was 200 times larger than the response of any interferences.

An Electrochemical Alcohol Sensor Based on a Co-electrodeposited Pt | WO₃ Electrode

Y. CHEN, K. Y. CHEN and A. C. C. TSEUNG, *J. Electroanal. Chem.*, 1999, **471**, (2), 151–155

A Pt|WO₃ electrode (1) was used for the rapid determination of EtOH in beer and wine. (1) was prepared by co-electrodeposition from a solution containing chloroplatinic acid and W onto a Au substrate of 0.5 cm² at -0.25 V for 30 min. The W solution was prepared by dissolving W powders in H₂O₂ followed by decomposing the excess H₂O₂ with a Pt foil coated with Pt black.

Electropolymerised Platinum Porphyrin Polymers for Dissolved Oxygen Sensing

A. S. HOLMES-SMITH, A. HAMILL, M. CAMPBELL and M. UTTAMLAL, *Analyst*, 1999, **124**, (10), 1463–1466

Sensitivities of poly-Pt tetraphenylporphyrin (1) and poly-Pt octaethylporphyrin (2) to dissolved O₂, given by Stern-Volmer quenching coefficients, were obtained from luminescence lifetime measurements as 1.12 (mg l⁻¹)⁻¹ and 2.07 (mg l⁻¹)⁻¹, respectively. The response time for (2), determined from luminescence intensity measurements, to a step change in O₂ concentration of 4.3–38.6 mg l⁻¹ was 8 ms. The limit of detection obtained for an O₂ sensor based on (2) was 0.06 mg l⁻¹.

Fabrication of Defect-Free Pd/ α -Al₂O₃ Composite Membranes for Hydrogen Separation

A. LI, W. LIANG and R. HUGHES, *Thin Solid Films*, 1999, **350**, (1, 2), 106–112

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

B. MCCOOL, G. XOMERITAKIS and Y. S. LIN, *J. Membrane Sci.*, 1999, **161**, (1–2), 67–76

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^{-8} to 1×10^{-7} mol m⁻²s⁻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

I. V. YENTEKAKIS, M. KONSOLAKIS, R. M. LAMBERT, N. MACLEOD and L. NALBANTIAN, *Appl. Catal. B: Environ.*, 1999, **22**, (2), 123–133

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, while 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-Pt-Ce/Alumina Catalyst

Q. ZHANG and K. T. CHUANG, *Environ. Sci. Technol.*, 1999, **33**, (20), 3641–3644

Pd-Pt-Ce/Al₂O₃ (1) shows promising activity over traditional Fe₂O₃, 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 PtCl₄ Ion Pair as a Recycle Hydrogenation Catalyst

M. SETTY-FICHMAN, K. KUPFERMAN, V. BATZ, C. ROTTMAN, Y. SASSON and J. BLUM, *J. Mol. Catal. A: Chem.*, 1999, **144**, (1), 159–163

Polystyrene-supported ion pairs formed from PtCl₄ 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

M. T. REETZ and M. G. KOCH, *J. Am. Chem. Soc.*, 1999, **121**, (34), 7933–7934

The hydrolysis/condensation of PtCl₄ or H₂PtCl₆ under basic conditions in the presence of carbo- or sulfobetaine stabilisers was shown to be a simple route to preparing H₂O-soluble, stable, nanosized colloidal PtO₂. 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 PtRuO_x 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

D. GAŠPAROVICOVÁ, M. KRÁLIK and M. HRONEC, *Collect. Czech. Chem. Commun.*, 1999, **64**, (3), 502–514

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 reaction 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

G. PECCHI, P. REYES, F. ORELLANA, T. LÓPEZ, R. GÓMEZ and J. L. G. FIERRO, *J. Chem. Technol. Biotechnol.*, 1999, **74**, (9), 897–903

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 Cl⁻, 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

C. BIANCHINI, H. M. LEE, P. BARBARO, A. MELI, S. MONETTI and F. VIZZA, *New J. Chem.*, 1999, **23**, (9), 929–938

[Pd(P-P)(N-N)](PF₆)₂ (P-P = 1,3-bis(diphenylphosphino)propane, *meso*-2,4-bis(diphenylphosphino)pentane (*meso*-bdpp), *rac*-2,4-bis(diphenylphosphino)pentane, 2,2'-bis(diphenylphosphinoethyl)pentane; 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*-bdpp)(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 Chlorotris(1,3,5-triaza-7-phosphaadamantane)-rhodium(I) Complex Catalyst

L. NÁDASDI and F. JOÓ, *Inorg. Chim. Acta*, 1999, **293**, (2), 218–222

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 diduterated 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 Hydroaminomethylation with Ammonia: With Dual Metal Catalysts and Two-Phase Catalysis to Primary Amines

B. ZIMMERMANN, J. HERWIG and M. BELLER, *Angew. Chem. Int. Ed.*, 1999, **38**, (16), 2372–2375

The highly selective hydroaminomethylation 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

G. FRANCIÓ and W. LEITNER, *Chem. Commun.*, 1999, (17), 1663–1664

The use of a Rh catalyst with a new perfluoroalkyl-substituted (*R,S*)-H⁺-BINAPHOS ligand (1) has allowed the efficient and highly regio- and enantioselective hydroformylation of vinyl arenes in compressed CO₂. Similar catalytic activity and the same level of enantiocontrol as (*R,S*)-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

D. HOEGAERTS and P. A. JACOBS, *Tetrahedron: Asymmetry*, 1999, **10**, (15), 3039–3043

(*R*)-BINAP-Rh(I) complexes derived from Rh(acac)(CO)₂ and [Rh(μ-OMe)(cod)]₂ 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)₃³⁺ Oxidant

T. ABE, Y. TAMADA, H. SHIROISHI, M. NUKAGA and M. KANEKO, *J. Mol. Catal. A: Chem.*, 1999, **144**, (3), 389–395

In a catalytic H₂O oxidation system composed of Ru(bpy)₃³⁺ and RuO₂ adsorbing Ru-red, a much higher amount of O₂ evolved than in a homogeneous Ru(bpy)₃³⁺/Ru-red system. The amount of O₂ evolved increased with the amount of Ru-red adsorbed in RuO₂, but higher amounts of adsorbed 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

P. D. BEATTIE, V. I. BASURA and S. HOLDCROFT, *J. Electroanal. Chem.*, 1999, **468**, (2), 180–192

Kinetic 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 Pd₃Ge formation, transformation into PdGe and excess Ge crystallisation. For good ohmic contact, Ge transport to the interface with GaAs is the key.