

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

High Temperature Phase Transitions in $\text{Al}_{1+x}\text{Pt}_{3-x}$

W. BRONGER, K. WRZESIEN and P. MÜLLER, *Solid State Ionics*, 1997, **101–103**, 633–640

Pt-rich Al-Pt alloys were produced from the reaction of Al oxide and Pt in H_2 at 1200°C. Upon heating, alloys with a slight tetragonal distortion underwent a second order phase transition into a cubic phase, while alloys with a stronger tetragonal distortion underwent a corresponding first order phase transition. In the former case this distortion was progressively relieved with increasing temperature, but discontinuously in the latter case.

Structure and Chemical Composition of Surfactant-Stabilized PtRu Alloy Colloids

W. VOGEL, P. BRITZ, H. BÖNNEMANN, J. ROTHE and J. HORMES, *J. Phys. Chem. B*, 1997, **101**, (51), 11029–11036

In situ XRD was used to study unsupported and SiO_2 -supported clusters of $\text{PtRu}[\text{N}(\text{Oct}), \text{Cl}]_3$ (Pt:Ru ~ 1:1). The best fit simulation for the unsupported clusters gives a 50/50 mixture of colloid particles with f.c.c. symmetry and multiply twinned decahedral particles. The SiO_2 -supported colloid particles oxidised rapidly in air to form an amorphous state but could be re-reduced in H_2 at room temperature.

Permeability of Hydrogen in Amorphous $\text{Pd}_{(1-x)}\text{Si}_x$ Alloys at Elevated Temperatures

N. ITOH, W.-C. XU, S. HARA, H. M. KIMURA and T. MASUMOTO, *J. Membrane Sci.*, 1998, **139**, (1), 29–35

H_2 permeabilities of amorphous $\text{Pd}_{(1-x)}\text{Si}_x$ ($x = 0.15, 0.175, 0.2$) alloys, formed as ribbons by a single roller spinning technique, were measured at $\leq 390^\circ\text{C}$. The H_2 permeability decreased with increasing Si content and the amorphous alloys had 3–5 times higher permeability than corresponding crystallised alloys.

A New Molecular Superconductor β' - $\text{Et}_2\text{Me}_2\text{P}[\text{Pd}(\text{dmit})_2]_2$ (dmit = 2-thioxo-1,3-dithiole-4,5-dithiolate)

R. KATO, Y. KASHIMURA, S. AONUMA, N. HANASAKI and H. TAJIMA, *Solid State Commun.*, 1998, **105**, (9), 561–565

The anion radical salt β' - $\text{Et}_2\text{Me}_2\text{P}[\text{Pd}(\text{dmit})_2]_2$ is non-metallic at ambient pressure but metallic under pressure with a superconducting transition in the range 6.9–10.4 kbar with $T_c = 4.0$ –1.8 K (onset). At higher pressures it is non-metallic at low temperature. The isostructural salt β' - $\text{Et}_2\text{Me}_2\text{Sb}[\text{Pd}(\text{dmit})_2]_2$ also shows pressure induced metallic behaviour, but no superconducting transition above 1.6 K, and remains metallic at pressures up to 16.4 kbar.

Phase Formation Process of $\text{Ir}_x\text{Si}_{1-x}$ Thin Films. Structure and Electrical Properties

R. KURT, W. PITSCHKE, A. HEINRICH, J. SCHUMANN, J. THOMAS, K. WETZIG and A. BURKOV, *Thin Solid Films*, 1997, **310**, (1, 2), 8–18

Phase formation processes in amorphous $\text{Ir}_x\text{Si}_{1-x}$ thin films with $0.30 \leq x \leq 0.41$ were studied in relation to electric transport properties. Distinct phases were observed depending on the initial composition: Ir_3Si_4 , Ir_2Si_3 and IrSi_2 . However, for a Si concentration of 61–64 at.%, an unknown metastable phase was found in films after annealing above the crystallisation temperature of 970 K. This was found to be monoclinic, b.f.c. with lattice constants $a = 1.027$ nm, $b = 0.796$ nm, $c = 0.609$ nm and $\gamma = 113.7^\circ$.

The Optical Properties of RuSi: Kondo Insulator or Conventional Semiconductor?

V. VESCOLI, L. DEGIORGI, B. BUSCHINGER, W. GUTH, C. GEIBEL and F. STEGLICH, *Solid State Commun.*, 1998, **105**, (6), 367–370

Single-phase RuSi acts as a simple metal in its high temperature phase (CsCl type). In its low temperature phase (FeSi type) it is a semiconductor with a narrow band gap of ~ 0.4 eV at room temperature and an even smaller gap of ~ 20 meV in the optical spectra below 100 K. Its physical properties are strongly influenced by impurities and stoichiometric deviations and resemble those of a heavily doped semiconductor.

CHEMICAL COMPOUNDS

The Preparation and Crystal and Molecular Structure of the Complex *cis*- $\text{PtCl}_2(\text{razoxane})$

H. O. DAVIES, D. A. BROWN, A. I. YANOVSKY and K. B. NOLAN, *Inorg. Chim. Acta*, 1998, (2), 313–316

Treatment of the anti-cancer drug razoxane (3,5-dioxo-piperazin-1-yl-propane) (1) with $\text{K}_2[\text{PtCl}_4]$ in aqueous HCl gave *cis*- $\text{PtCl}_2(\text{razoxane})$, which is the first metal complex of (1) reported. (1) is co-ordinated as a bidentate ligand and was not hydrolysed during the reaction. The complex is unusual as the Pt is bonded to the ligand via tertiary N atoms only.

Synthesis and Structural Characterization of an Authentic Platinum(IV) Carbonyl Compound

J. FORNIES, M. A. GÓMEZ-SASO, A. MARTÍN, F. MARTÍNEZ, B. MENJÓN and J. NAVARRETE, *Organometallics*, 1997, **16**, (26), 6024–6027

Oxidative addition of Br_2 to $[\text{NBu}_4]_2[\text{Pt}(\text{C}_6\text{F}_5)_4]$ followed by halide extraction with AgClO_4 in the presence of CO gave $[\text{NBu}_4][\text{trans-Pt}^{\text{IV}}(\text{C}_6\text{F}_5)_4\text{Br}(\text{CO})]$. This is the first structurally characterised Pt(IV) carbonyl derivative with a mainly σ -donor CO ligand.

Synthesis and Characterization of Palladium and Nickel Complexes with Positively Charged Triphosphine Ligands and Their Use as Electrochemical CO₂-Reduction Catalysts

A. MIEDANER, B. C. NOLL and D. L. DUBOIS, *Organometallics*, 1997, 16, (26), 5779–5791

The synthesis of [Pd(Bu₃P⁺etpE)Br](BF₄)₂ (Bu₃P⁺etpE = [(Bu₃PCH₂CH₂)P(CH₂CH₂PEt₂)₂]⁺) (1) and [Pd(etpPBu₃⁺)Br]Br(BF₄)₂ (etpPBu₃⁺ = {PhP[CH₂-CH₂P(CH₂CH₂PBu₃)₂]⁺})⁴⁺ is described. Treatment of (1) with AgBF₄ in CH₃CN gave [Pd(Bu₃P⁺etpE)-(CH₃CN)](BF₄)₃, which, along with [Pd(Me₃P⁺etpE)-(CH₃CN)](BF₄)₃, is a catalyst for the electrochemical reduction of CO₂ to CO.

ELECTROCHEMISTRY

Cleavage of the C-C Bond during the Electrooxidation of 1-Propanol and 2-Propanol: Effect of the Pt Morphology and of Codeposited Ru

I. DE A. RODRIGUES, J. P. I. DE SOUZA, E. PASTOR and F. C. NART, *Langmuir*, 1997, 13, (25), 6829–6835

The electrooxidation of 1-propanol (1) and 2-propanol (2) was studied on smooth Pt and electrodeposited Pt and Pt_{0.89}Ru_{0.11}. On smooth Pt, partially oxidised products were detected, propionic acid from (1) and acetone from (2), as well as CO₂. For (1), CO₂ production increased as the roughness of the electrode increased (electrodeposited Pt) and propionic acid production was totally eliminated on the Pt_{0.89}Ru_{0.11} alloy. For (2), acetone formation was inhibited on the electrodeposited Pt but no additional effects were noted on the Pt_{0.89}Ru_{0.11}.

A Novel Polymer Electrolyte Based on Oligo(Ethylene Glycol) 600, K₂PdCl₄ and K₃Fe(CN)₆

V. D. NOTO, *J. Mater. Res.*, 1997, 12, (12), 3393–3402
Polymer electrolytic systems were prepared by reacting K₃Fe(CN)₆ and K₂PdCl₄ in a mixture of H₂O and poly(ethylene glycol) 600 (PEG). This reaction occurs in two steps: formation of a gel, then shrinkage to release the solvent. The product is very stable and has the consistency of a smooth, solid plastic paste. The polymer synthesised with the highest PEG 600:H₂O ratio had a conductivity of ~ 1.4 × 10⁻³ S cm⁻¹ at 25°C. This is ~ 2 orders of magnitude higher than those of Li polymer electrolytes used in rechargeable batteries.

Catalytic Behaviour of Osmium(II), Rhodium(III) and Ruthenium(II) Phthalocyanines Towards the Electrooxidation of Cysteine on Glassy Carbon Electrodes

M. SEKOTA and T. NYOKONG, *Electroanalysis*, 1997, 9, (16), 1257–1261

Glassy carbon electrodes modified with phthalocyanine complexes: (DMSO)(Cl)Rh^{III}Pc, [(CN)₂Rh^{III}Pc]₂, (DMSO)₂Os^{III}Pc and [(DMSO)₂Ru^{II}Pc]₂DMSO were autocatalytic for the oxidation of cysteine. This is attributed to the formation of dimeric π cation radical species at the electrode surface.

Electrochemical Behaviour of [Ru(4,4'-Me₂bpy)₂(PPh₃)(H₂O)](ClO₄)₂ in Homogeneous Solution and Incorporated into a Carbon Paste Electrode. Application to Oxidations of Benzylic Compounds

E. C. LIMA, P. G. FENGA, J. R. ROMERO and W. F. DE GIOVANI, *Polyhedron*, 1998, 17, (2–3), 313–318

The catalytic activity of [Ru(4,4'-Me₂bpy)₂(PPh₃)(H₂O)](ClO₄)₂ (1) was studied during the homogeneous electrooxidation of benzylic compounds. Reactivity decreased in the order 1-phenylethanol >> phthalic alcohol > benzyl alcohol > 4-methylbenzyl alcohol > ethylbenzene > toluene. C paste electrodes containing (1) also showed catalytic activity.

PHOTOCONVERSION

Interaction of Iridium Trihydridophosphine Complex with Fullerene C₆₀ under Thermal and Photochemical Stimulation

N. F. GOLDSHLEGER, N. N. DENISOV, V. A. NADTOCHENKO, M. G. KAPLUNOV and A. V. KULIKOV, *Izv. RAN, Ser. Khim.*, 1997, (12), 2145–2148

The interaction of H₃Ir(PPh₃)₃ (1) with C₆₀ under thermal and photochemical stimulation was studied under anaerobic conditions. Heating of a (1)-C₆₀ mixture (~1:1) or excitation by visible light resulted in new absorption bands characteristic of an η²-co-ordinated C₆₀ in a fullerene-containing metal complex.

Interactions between Positively Charged Starburst Dendrimers and Ru(4,7-(SO₃C₆H₅)₂-phen)₃⁴⁺

P. F. SCHWARZ, N. J. TURRO and D. A. TOMALIA, *J. Photochem. Photobiol. A: Chem.*, 1998, 112, (1), 47–52

The emission intensity and emissive lifetimes of Ru(4,7-(SO₃C₆H₅)₂-phen)₃⁴⁺ (1) were studied in solutions containing various cationic starburst dendrimers (SBD) with and without potential quenchers. Binding constants of (1) to SBD were determined by changes in the probe's excited state lifetime. An increase in the probe lifetime was observed in the presence of SBD. The quenching constants between (1) and methylviologen (MV²⁺), K₃Fe(CN)₆ and K₂Fe(CN)₆ were determined by laser flash-photolysis.

Photoaddition of Ru(tap)₂(bpy)²⁺ to DNA: A New Mode of Covalent Attachment of Metal Complexes to Duplex DNA

L. JACQUET, R. J. H. DAVIES, A. KIRSCH-DE MESMAEKER and J. M. KELLY, *J. Am. Chem. Soc.*, 1997, 119, (49), 11763–11768

Covalent adducts with guanine were formed by near-UV or visible light irradiation of Ru(tap)₂(bpy)²⁺ (1) (tap = 1,4,5,8-tetraazaphenanthrene; bpy = 2,2'-bipyridyl) with duplex DNA. The adduct was isolated as both its nucleotide and nucleobase derivatives. Two isomeric covalent adducts were formed in which the exocyclic amino group of a guanine nucleobase was linked to the C2 or C7 position of one of the tap ligands. This is a new type of site specific modification of DNA by a photoexcited Ru complex.

ELECTRODEPOSITION AND SURFACE COATINGS

Defect-Free Palladium Membranes on Porous Stainless-Steel Support

P. P. MARDILOVICH, Y. SHE, Y. H. MA and M.-H. REI, *AICHe J.*, 1998, **44**, (2), 310–322

Defect-free Pd membranes were prepared by an electroless plating technique on porous stainless steel tubes. The effective surface of Pd membranes was $\leq 75 \text{ cm}^2$ and H_2 permeances of $\leq 8 \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1} \text{ atm}^{0.5}$ were achieved at 350°C . No He flux was detected at room temperature and a pressure difference of 3 atm. At a pressure difference of 1 atm and at 350°C , selectivity coefficients (H_2/N_2) of 5000 and H_2 fluxes $\leq 4 \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1}$ were observed. The membranes were stable at 350°C for 1100 h, with no significant changes in the steady-state H_2 flux, leading to a recrystallisation texture and aggregation of Pd grains.

Cathodic Electrosynthesis of Titanium and Ruthenium Oxides

I. ZHITOMIRSKY, *Mater. Lett.*, 1998, **33**, (5, 6), 305–310

The electrosynthesis of RuO_2 , TiO_2 and composite RuO_2 - TiO_2 films on Pt substrates was performed cathodically via hydrolysis of TiCl_4 and $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ salts dissolved in H_2O or mixed $\text{MeOH-H}_2\text{O}$. The films can be obtained as monolayers or multilayers, as the amount of deposited material and its composition can be controlled. The crystallisation behaviour of the deposits and a possible mechanism of electrosynthesis are discussed.

APPARATUS AND TECHNIQUE

SnO_2 and SnO_2 :Pt Thin Films Used as Gas Sensors

M. DE LA L. OLVERA and R. ASOMOZA, *Sens. Actuators B*, 1997, **45**, (1), 49–53

Thin films of SnO_2 ($< 20 \text{ nm}$) and SnO_2 :Pt, prepared by chemical spray deposition on glass substrates at various temperatures, have been assessed as CO gas sensors. Ultrathin SnO_2 :Pt films with an amorphous structure were found to be highly sensitive, with an optimum Pt concentration of $\sim 3 \text{ at.}\%$ in the starting solution. Sensitivities of 5 for SnO_2 and $\sim 4 \times 10^2$ for SnO_2 :Pt were obtained in the presence of 3.8 torr of CO partial pressure.

Study on Fence-Free Platinum Etching Using Chlorine-Based Gases in Inductively Coupled Plasma

C. W. CHUNG and H. G. SONG, *J. Electrochem. Soc.*, 1997, **144**, (11), L294–L296

A Cl_2/Ar gas combination, in an inductively coupled plasma, was successfully used to etch Pt thin films without redeposition of etch products. Most of the redeposited material formed on the pattern sidewall was determined to be PtCl_2 by X-ray photoelectron spectroscopy and secondary ion mass spectroscopy. The addition of SiCl_4 to the gas enhanced the formation of volatile compounds and significantly reduced redeposition to give a clean etch profile for the Pt films.

Improved Response Time of Al- Al_2O_3 -Pd Tunnel Diode Hydrogen Gas Sensor

S. OKUYAMA, H. USAMI, K. OKUYAMA, H. YAMADA and K. MATSUSHITA, *Jpn. J. Appl. Phys.*, 1997, **36**, (11), 6905–6908

An Al- Al_2O_3 -Pd tunnel diode acts as a sensitive H_2 gas sensor at room temperature but exhibits a very long response time of 30 min. However, at elevated temperature, a marked reduction in the response time, to $< 1 \text{ min}$ at 83°C , was achieved for 0.01 torr H_2 . A microheater attached to the back face of the substrate could efficiently heat the H_2 sensor.

Fluorescent Organofilms for Oxygen Sensing in Organic Solvents Using a Fiber Optic System

N. VELASCO-GARCÍA, M. J. VALENCIA-GONZÁLEZ and M. E. DÍAZ-GARCÍA, *Analyst*, 1997, **122**, (11), 1405–1409

O_2 concentrations in organic solvents can be determined by the luminescence quenching of $[\text{Ru}(\text{bpy})_3]^{2+}$ entrapped in gelatin-containing microemulsion-based organogels. A fibre optic design combined with a continuous flow system configuration gave a dynamic response of $< 1 \text{ min}$ for a full signal change. A detection limit of 0.2 ppm O_2 was measured in hexane-5% chloroform; the organogel phase was highly photostable, showing no degradation after $> 20 \text{ h}$ of continuous illumination.

Polymer-Supported pH Sensors Based on Hydrophobically Bound Luminescent Ruthenium(II) Complexes

J. M. PRICE, W. XU, J. N. DEMAS and B. A. DEGRAFF, *Anal. Chem.*, 1998, **70**, (2), 265–270

Luminescence intensity-based pH sensors are described based on $[\text{Ru}(\text{phen})_2[\text{phen}(\text{OH})_2]]^{2+}$ (1) or $[\text{Ru}(\text{Ph}_2\text{phen})_2[\text{phen}(\text{OH})_2]]^{2+}$ (2) (phen = 1,10-phenanthroline, Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, and $\text{phen}(\text{OH})_2$ = 4,7-dihydroxy-1,10-phenanthroline) immobilised on siloxane ring polymers. These systems work over the pH range of ~ 1 –6 with (1) and 2–8 with (2). Response times for thick films ($250 \mu\text{M}$) are rapid (several minutes).

HETEROGENEOUS CATALYSIS

Methanation of K^+ -Modified Pt/ SiO_2 : the Impact of Reaction Conditions on the Effective Role of the Promoter

I.-G. BAJUSZ, D. J. KWIK and J. G. GOODWIN, *Catal. Lett.*, 1997, **48**, (3, 4), 151–157

The effect of alkali promotion on Pt methanation was studied on a 4.5 wt.% Pt/ SiO_2 catalyst promoted with K^+ ($\text{K}^+:\text{Pt} = 0, 0.1$ and 0.2) over two temperature ranges. The methanation rate was 10–70% lower on the promoted catalysts at 573–665 K and not dependent on temperature or other variables. At 503–552 K the promoted catalyst had a higher methanation activity and lower activation activity for all temperatures and partial pressures of H_2 and CO. The catalyst with a $\text{K}^+:\text{Pt}$ ratio of 0.1 showed the highest methanation activity. It is concluded that K^+ acts as a rate promoter at the lower reaction temperatures but only as a site blocking agent at the higher temperatures.

Effect of Fluorination of Alumina Support on Activity of Platinum Catalysts for Complete Oxidation of Benzene

K. T. CHUANG, A. A. DAVYDOV, A. R. SANGER and M. ZHANG, *Catal. Lett.*, 1997, **49**, (3, 4), 155–161

A hydrophobic Pt-F/Al₂O₃ catalyst (1) was more active for the total oxidation of benzene than a hydrophilic Pt/Al₂O₃ catalyst (2) with the same Pt loading. (1) contained well-dispersed small Pt particles, in contrast to the larger particles on (2), with the high dispersion being due to a strong interaction of the metal particles with strong electron-acceptor sites formed by the fluorination of Al₂O₃.

Study on Catalysts for Methanol-Fuelled Vehicle Exhaust Control. 1. Deep Oxidation of Methanol on Pd-Al₂O₃

B. ZHU and R. WANG, *J. Fuel Chem. Technol. (China)*, 1997, **25**, (6), 531–538

Studies of Pd/ γ -Al₂O₃ catalysts used for the low temperature deep oxidation of MeOH showed them to be highly active with good selectivity. A 0.1% Pd/ γ -Al₂O₃ catalyst, prepared by impregnating (NH₄)₂PdCl₄ precursor solution into the γ -Al₂O₃ powder, followed by calcination in a reducing gas, had the highest activity in the absence of CO. The yields of partial oxidation products were low, and components of the feed gas, such as O₂ and CO, strongly affected the activity and selectivity of the reaction.

Pd/ δ -Al₂O₃ Catalysts for Isoprene Selective Hydrogenation: Regeneration of Water-Poisoned Catalysts

J.-R. CHANG, T.-B. LIN and C.-H. CHENG, *Ind. Eng. Chem. Res.*, 1997, **36**, (12), 5096–5102

Isoprene containing H₂O was partially hydrogenated over Pd/ δ -Al₂O₃ eggshell catalysts with a weight-hourly space velocity of 18 h⁻¹ at 40°C and 30 atm total pressure. The isoprene conversion decreased with time on stream. Catalyst activity loss was not restored by the introduction of H₂O-free isoprene, however, H₂ pretreatment reactivated the H₂O-poisoned catalyst, by increasing the number of Pd sites available for CO chemisorption. At nearly steady state, the isoprene conversion by catalysts reactivated at 200°C was ~93% of that by catalysts without H₂O-poisoning.

Investigation of the State of Palladium in the Pd/SO₄/ZrO₂ System by Diffuse-Reflectance IR Spectroscopy

A. V. IVANOV and L. M. KUSTOV, *Izv. RAN, Ser. Khim.*, 1998, (1), 57–61

Pd/ZrO₂ and Pd/SO₄/ZrO₂ systems were studied by diffuse-reflectance IR-spectroscopy using CO as a probe molecule. The Pd/ZrO₂ system showed a weak metal-support interaction which was increased by modification of the ZrO₂ support with SO₄²⁻ anions, as was the stability of the metal towards reduction. Surfaces modified by SO₄²⁻ anions contained the positively charged metal particles Pd⁺ and Pd^{δ+}. Acidic protons and surface sulfur compounds influenced the metal state, with smaller metal clusters having a higher charge on the sulfur atom.

Structure of Rh-Mo-K/Al₂O₃ Catalysts and Their Activity for Alcohol Synthesis

Z. LI, Y. FU and M. JIANG, *Chinese J. Catal.*, 1998, **19**, (1), 29–32

A series of Rh-Mo-K/Al₂O₃ catalysts was prepared with Rh loadings of 0–1.0% and a constant Mo and K content. The addition of 0.2% Rh into the oxidised Mo-K/Al₂O₃ system resulted in the aggregation of surface K-Mo species, while higher amounts of Rh gave an increased dispersion of the K-Mo species. The addition of Rh into the sulfided Mo-K/Al₂O₃ system improved both the selectivity for mixed alcohols and the activity of the catalyst, and shifted the distribution of oxygenates towards higher alcohols.

Impact of Molecular Order in Langmuir-Blodgett Films on Catalysis

K. TÖLLNER, R. POPOVITZ-BIRO, M. LAHAV and D. MILSTEIN, *Science*, 1997, **278**, (5346), 2100–2102

Catalytically active LB films of a Rh complex, prepared from the reaction of 4,4'-diheptadecyl-2,2'-bipyridine with [Rh(hexadiene)Cl]₂, were prepared to determine the effect of the molecular order of metal complexes on catalytic activity. The LB films were highly active for the hydrogenation of carbon-oxygen double bonds, whereas in a homogeneous solution the Rh complex exhibited low activity. The catalyst also showed remarkably high substrate selectivity and was highly dependent on the order and orientation of the films. Above 30°C, however, catalytic activity decreased but was reversible on cooling.

HOMOGENEOUS CATALYSIS

Synthesis of Unsymmetrical Triarylamines for Photonic Applications via One-Pot Palladium-Catalysed Aminations

S. THAYUMANAVAN, S. BARLOW and S. R. MARDER, *Chem. Mater.*, 1997, **9**, (12), 3231–3235

Unsymmetrically substituted triarylamines were prepared in multigram quantities by a high-yielding one-pot procedure, by sequentially adding two aryl bromides to an arylamine in the presence of Pd₂(dba)₃ (dba = dibenzylideneacetone). This method can be used to synthesise a number of analogues of 4,4'-bis(*m*-tolylphenylamino)biphenyl which may find use as the hole transport component of vapour-deposited organic light-emitting diodes.

A New Route to Concentrated Microlatex of Homogeneous Particle Size: Oligomerization of Norbornene in Aqueous Emulsion Catalyzed by PdCl₂

L. PUECH, E. PEREZ, I. RICO-LATTES, M. BON and A. LATTES, *New J. Chem.*, 1997, **21**, (11), 1235–1242

Norbornene was polymerised in aqueous micellar solutions of Na dodecyl sulfate (SDS) using PdCl₂ as the catalyst. This gave small latex particles ~10 nm in size consisting of oligomers of norbornene, whereas the reaction in pure H₂O precipitated high molecular weight polymers. This emulsion system was adapted to give a continuous process with a turnover of 70 moles of norbornene h⁻¹ mole⁻¹ of catalyst.

Catalysis of Giant Palladium Cluster Complexes. Highly Selective Oxidations of Primary Allylic Alcohols to α,β -Unsaturated Aldehydes in the Presence of Molecular Oxygen

K. KANEDA, Y. FUJIE and K. EBITANI, *Tetrahedron Lett.*, 1997, **38**, (52), 9023–9026

The giant Pd cluster Pd₃₆₁phen₆₀(OAc)₁₈₀ (phen = 1,10-phenanthroline) (1) is highly catalytic for the selective oxidations of primary allylic alcohols to the corresponding α,β -unsaturated aldehydes in the presence of O₂ under mild reaction conditions. (1) can also be anchored to TiO₂ to give an effective heterogeneous cluster catalyst for the above reactions which can be easily separated from the reaction mixtures and reused with minimal loss of activity and selectivity.

Homogeneous Catalysis in Liquefied Gas. Complex-Catalyzed Selective and Direct Conversion of Propane to Butanal at Room Temperature

T. SAKAKURA, K. ISHIGURO, M. OKANO and T. SAKO, *Chem. Lett. Jpn.*, 1997, (11), 1089–1090

Upon illumination with a high pressure mercury lamp, RhCl(CO)(PMe₃)₂ catalyses the carbonylation of liquefied propane at room temperature to yield butanal with high regioselectivity, giving an *n:iso* ratio of 98:2 after 48 h at 15°C. Turnover rates can be improved by increasing the relative irradiation intensity.

Influence of the Reaction Temperature on the Regioselectivity in the Rhodium-Catalyzed Hydroformylation of Vinylpyrroles

A. CAIAZZO, R. SETTAMBOLO, G. UCCELLO-BARRETTA and R. LAZZARONI, *J. Organomet. Chem.*, 1997, **548**, (2), 279–284

The influence of temperature on the regioselectivity in the hydroformylation of vinylpyrrole isomers and the corresponding *N*-tosylated substrates is reported at 20–100°C in the presence of Rh₄(CO)₁₂. The proportion of branched aldehyde was always higher (α -regioselectivity) but the amount of linear aldehyde increased as the temperature rose. ²H NMR studies showed that this behaviour is connected to a β -hydride elimination process occurring at high temperature for the branched alkyl-rhodium intermediate only.

Synthesis of Columnar Polyacetylenes by Rh Complex Catalyst

M. TABATA, T. SONE, Y. SADAHIRO, W. YANG, S. KOBAYASHI, Y. INABA and K. YOKOTA, *Kobunshi Ronbunshu*, 1997, **54**, (12), 863–874

A highly stereoregular polymerisation of phenylacetylene and its homologues was performed using a Rh catalyst, such as [Rh(norbornadiene)Cl]₂, in the presence of Et₃N or alcohol, giving polyacetylenes with a high *cis* content. The solvents dissociated the dimer complex catalyst to generate monomeric species as a possible propagation species for the polymerisation. A pressure induced *cis-trans* isomerisation generated fairly long *trans* conjugate sequences when pressure was exerted on the aromatic polyacetylene polymer at room temperature under vacuum.

Reduction of Amides to Amines via Catalytic Hydrosilylation by a Rhodium Complex

R. KUWANO, M. TAKAHASHI and Y. ITO, *Tetrahedron Lett.*, 1998, **39**, (9), 1017–1020

The reduction of a wide range of tertiary amides with 2 molar equivalents of Ph₂SiH₂ in the presence of 0.1 mol% RhH(CO)(PPh₃)₃ (1) at room temperature gave the corresponding tertiary amines in high yields. Amides with bromo, ester or epoxy functional groups were reduced chemoselectively, in contrast to conventional reductions with LiAlH₄ and/or BH₃, although amides with C–C double and triple bonds and α -active methylene gave complicated mixtures. Primary and secondary amides did not react with hydrosilane in the presence of (1).

Stereoselective Metal Catalysed Hydroboration of 4-Substituted 1-Methylidenecyclohexanes

X.-L. HOU, Q.-C. XIE and L.-X. DAI, *J. Chem. Res. (S)*, 1997, (12), 436

The hydroboration of 4-substituted 1-methylidenecyclohexanes in the presence of a Rh catalyst gives *cis*-4-substituted cyclohexane-1-methanols in high yield and stereoselectivity. This system gave a *cis:trans* ratio of 13.3:1 under catalytic conditions, compared to a ratio of ~ 1–2:1 obtained from conventional hydroboration. The best results were obtained with Rh catalysts prepared in situ by reacting [Rh(COD)Cl]₂ with 4 equiv. of PPh₃.

Synthesis, X-ray Structure, and Catalytic Activity of the Unusual Complex [Ir(TFB)(PiPr₃)₂]BF₄ (TFB = Tetrafluorobenzobarrelene)

W. CHEN, M. A. ESTERUELAS, J. HERRERO, F. J. LAHOZ, M. MARTÍN, E. OÑATE and L. A. ORO, *Organometallics*, 1997, **16**, (26), 6010–6013

IrCl(TFB)(PiPr₃) (TFB = tetrafluorobenzobarrelene) reacts with AgBF₄ in the presence of triisopropylamine to give [Ir(TFB)(PiPr₃)₂]BF₄ (1) in 93% yield. This complex reacts with H₂ to give *cis-trans*-[IrH₂(TFB)(PiPr₃)₂]BF₄ in 87% yield, which is also an active catalyst for the hydrogenation of a variety of olefins, including styrene. Although (1) reacts with phenylacetylene to give Ir(C₂Ph)(TFB)(PiPr₃), it catalyses the hydrogenation of alkynes to alkenes in dichloromethane, giving selectivities close to 80% at 25°C and atmospheric pressure.

A New Ruthenium-Catalyzed Reaction with Propargyl Alcohol: Cyclopropanation of Norbornene

H. KIKUCHI, M. UNO and S. TAKAHASHI, *Chem. Lett. Jpn.*, 1997, (12), 1273–1274

The reaction of propargyl alcohol and norbornene was catalysed by cationic (η^1 -cyclopentadienyl)-tris(acetonitrile)Ru complexes to give a cyclopropanation product, acetyltricyclooctane, in excellent yield. The Ru-catalysed reaction of 2-propyn-1-ol with norbornene proceeded smoothly at room temperature in alcoholic solvents, with methanol being the best choice, although almost no reaction occurred in benzene, THF or dichloromethane.

Asymmetric Hydrosilylation of Ketones Catalyzed by Ruthenium Complexes with Chiral Tridentate Ligands

G. ZHU, M. TERRY and X. ZHANG, *J. Organomet. Chem.*, 1997, **547**, (1), 97–101

A new chiral ligand containing two phosphines and one pyridine is highly effective for the Ru-catalysed hydrosilylation of simple ketones. Using 1 mol% of a Ru catalyst, such as $[\text{RuCl}_2(\text{C}_6\text{H}_5)_2]$, and 2.2 mol% of the chiral tridentate ligand, enantioselectivities of 47–66% were obtained in yields of 85–98%.

FUEL CELLS

Reduction of Nitric Monoxide to Nitrogen at Gas Diffusion Electrodes with Pd Catalysts

N. FURUYA, K. MURASE and M. SHIBATA, *J. Electroanal. Chem.*, 1997, **436**, (1–2), 281–283

The electrochemical reduction of NO to N_2 was studied at a gas diffusion electrode with Pd catalysts for varying NO flow rates. At a flow rate of 5 ml min^{-1} the reaction occurs selectively at potentials $< 0.1 \text{ V}$, giving a current efficiency of ~95%. A H_2 -NO fuel cell reactor allows simultaneous electricity generation and NO decomposition, with a N_2 formation current efficiency of ~80% at a cell voltage of 0.25 V.

ELECTRICAL AND ELECTRONIC ENGINEERING

Variation of Electrical Conduction Phenomena of Pt/(Ba, Sr)TiO₃/Pt Capacitors by Different Top Electrode Formation Processes

K. H. LEE, C. S. HWANG, B. T. LEE, W. D. KIM, H. HORII, C. S. KANG, H.-J. CHO, S. I. LEE and M. Y. LEE, *Jpn. J. Appl. Phys.*, 1997, **36**, (9B), 5860–5865

Electrical properties of Pt/(Ba, Sr)TiO₃/Pt thin film capacitors with top Pt electrodes deposited at various deposition powers were studied before and after post-annealing in N_2 . The capacitor with a top Pt electrode deposited at 0.2 kW had Schottky emission behaviour under positive and negative biases, with interface potential barrier heights of 1.88–2.08 eV and 1.24–1.48 eV, respectively. However, for deposition at 0.5 kW, Schottky emission was observed only under positive bias at the bottom electrode at a barrier height of 1.61–1.89 eV.

Thermal Stability of the Non-Alloyed Pd/Sn and Pd/Ge Ohmic Contacts to n-GaAs

M. S. ISLAM, P. J. MCNALLY and D. C. CAMERON, *Thin Solid Films*, 1997, **308–309**, 607–610

The thermal stability of a non-alloyed Pd/Sn ohmic contact for n-GaAs was compared to a non-alloyed Pd/Ge metallisation. The Pd(50 nm)/Sn(125 nm) contacts (1) showed a lowest ρ_c of $2.28 \times 10^{-5} \Omega \text{ cm}^2$ which was higher than for similar Pd/Ge samples. The Pd/Sn ohmic contacts however showed superior thermal stability at 410°C; after annealing at 410°C for 4 h, the ρ_c of (1) remained in the low $10^{-5} \Omega \text{ cm}^2$ range whereas that of the Pd/Ge contacts increased by two orders of magnitude.

Improvement of Shape Memory Characteristics by Precipitation-Hardening of Ti-Pd-Ni Alloys

S. SHIMIZU, Y. XU, E. OKUNISHI, S. TANAKA, K. OTSUKA and K. MITOSE, *Mater. Lett.*, 1998, **34**, (1, 2), 23–29

Non-equiatomic Ti-Pd-Ni high temperature shape memory alloys (Ti:(Ni, Pd) \neq 50:50) were precipitation-hardened to improve their shape memory characteristics. For $\text{Ti}_{30.6}\text{Pd}_{30}\text{Ni}_{19.4}$ alloys, homogeneously distributed fine particles could be produced by ageing at 773 K. These precipitates increased the critical stress for slip and greatly improved the shape memory characteristics at high temperature.

Deposition of Ruthenium Nanoparticles on Carbon Aerogels for High Energy Density Supercapacitor Electrodes

J. M. MILLER, B. DUNN, T. D. TRAN and R. W. PEKALA, *J. Electrochem. Soc.*, 1997, **144**, (12), L309–L311

A new type of composite electrode using C aerogels as high surface area substrates for pseudocapacitive RuO_2 nanoparticles was prepared by the chemical vapour impregnation of Ru into C to produce a uniform distribution of adherent ~20 Å nanoparticles on the aerogel surface. The Ru particles dramatically improved the energy storage characteristics of the aerogel so that specific capacitances of $> 200 \text{ F g}^{-1}$ were obtained in comparison to 95 F g^{-1} for the untreated aerogel.

Electrical Properties of All-Perovskite Oxide (SrRuO₃/Ba_xSr_{1-x}TiO₃/SrRuO₃) Capacitors

M. IZUHA, K. ABE and N. FUKUSHIMA, *Jpn. J. Appl. Phys.*, 1997, **36**, (9B), 5866–5869

Perovskite oxide thin film capacitors ($\text{SrRuO}_3/\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3(20 \text{ nm})/\text{SrRuO}_3$) were fabricated on Si and SrTiO_3 substrates and their electrical properties studied. The relative dielectric constants for polycrystalline and single crystal epitaxial capacitors were 274 and 681, respectively. The lowest SiO_2 equivalent thickness for a single crystal epitaxial capacitor was 0.11 nm. The leakage current density was $< 1 \times 10^{-7} \text{ A cm}^{-2}$ for a $\pm 1.2 \text{ V}$ bias. Comparison of samples with SrRuO_3 and Pt top electrodes showed a large difference in the dielectric constants, which was attributed to differences in the interface between the dielectric and the top electrodes, and the existence of a low- ϵ layer.

MEDICAL USES

Synthesis, Structure, and Antimetastatic Activity of *trans*-[Pt(NC₅H₄C(O)NHC₂H₄ONO₂)₂Cl₂] Complex

I. L. EREMENKO, M. A. GOLUBNICHAYA, S. E. NEFEDOV, A. A. SIDOROV, D. A. NESTERENKO, N. P. KONOVALOVA, L. M. VOLKOVA and L. T. EREMENKO, *Izv. RAN, Ser. Khim.*, 1997, (9), 1672–1675

Complex *trans*-[Pt(NC₅H₄C(O)NHC₂H₄ONO₂)₂Cl₂] was prepared in H_2O by interacting K_2PtCl_4 with nicotandyl (*N*-nitroxynicotinamide), a complex used in cardiology. This complex displayed high antitumour activity, unlike a Br-containing Cu^{II} analogue.