

# ABSTRACTS

of current literature on the platinum metals and their alloys

## PROPERTIES

### Formation of Platinum Nanosheets between Graphite Layers

M. SHIRAI, K. IGETA and M. ARAI, *Chem. Commun.*, 2000, (7), 623–624

Pt nanosheets (thickness 2–3 nm) containing hexagonal holes were formed between graphite layers by H<sub>2</sub> reduction of PtCl<sub>4</sub>-graphite intercalation compounds. The intercalation reaction of PtCl<sub>4</sub> with graphite was performed at 723 K for 2 weeks under Cl<sub>2</sub> at 0.3 MPa.

### Comparison of Hydrogen Adsorption Abilities of Platinum-Loaded Carbon Fibres Prepared Using Two Different Methods

J. OZAKI, W. OHIZUMI, A. OYA, M. J. ILLAN-GOMEZ, M. C. ROMAN-MARTINEZ and A. LINARES-SOLANO, *Carbon*, 2000, 38, (5), 778–780

A polymer blend method (1) and a mixing method (2) were used to prepare Pt/C fibres. Using (1) gave Pt particles selectively deposited on the pore walls of the C fibre. At lower Pt loadings H spillover occurred giving a larger H:Pt ratio than expected from Freil's diagram. (2) gave a bimodal size distribution to the Pt particles. A lower Pt loaded sample of (2) had excellent H<sub>2</sub> adsorption due to the particle size (< 2–3 nm).

### Monodisperse FePt Nanoparticles and Ferromagnetic FePt Nanocrystal Superlattices

S. SUN, C. B. MURRAY, D. WELLER, L. FOLKS and A. MOSER, *Science*, 2000, 287, (5460), 1989–1992

Monodisperse FePt nanoparticles (diameter 3–10 nm) (1) were synthesised by reduction of Pt acetylacetonate and Fe(CO)<sub>5</sub> decomposition in the presence of stabilisers. Thermal annealing of (1) converted the self-assembled nanoparticle 3D superlattices into ferromagnetic nanocrystal assemblies which can support high-density magnetisation reversal transitions.

### Pressure-Induced Insulator-to-Metal-to-Insulator Transitions in One-Dimensional Bis(dimethylglyoximate)platinum(II), Pt(dmg)<sub>2</sub>

K. TAKEDA, I. SHIROTANI and K. YAKUSHI, *Chem. Mater.*, 2000, 12, (4), 912–916

Electrical resistivities, absorption spectra and XRD of 1D Pt(dmg)<sub>2</sub> (1) were investigated at high pressures. The resistivity drastically decreases with increasing pressure and reaches a minimum at ~ 6.5 GPa and then slowly increases with increasing pressure above this pressure. Pressure-induced insulator-to-metal-to-insulator (IMI) transitions in (1) were found at ~ 5 and 6 GPa. These transitions and the resistivity minimum arise from the change of the electronic states of (1) at high pressure.

### Activated Hydride Reduction of Palladium-Copper Ions in Organic Media: Formation of Nanocrystalline Pd-Cu Alloy Powders

S. ILLY-CHERREY, O. TILLEMENT, F. MASSICOT, Y. FORT, J. GHANBAJA and J. M. DUBOIS, *Mater. Sci. Eng.*, 2000, A283, (1–2), 11–16

Chemical reduction of Pd(II) and Cu(II) salts by activated alkaline hydride in THF at low temperature gave stable single-phase Pd<sub>x</sub>Cu<sub>100-x</sub> (0 ≤ x ≤ 100 at.%) nanoparticles (1) (1–10 nm). TEM of (1) showed homogeneous distribution of Pd and Cu. Good stabilisation against agglomeration was observed and such a polymetallic colloidal solution could be advantageously employed for catalytic impregnation.

### Hydrogen Isotherms for Following the Internal Oxidation of Ternary Pd Alloys

D. WANG, T. B. FLANAGAN and R. BALASUBRAMANIAM, *Scr. Mater.*, 2000, 42, (9), 911–915

Pd<sub>0.90</sub>Rh<sub>0.05</sub>Ni<sub>0.05</sub> alloy foil (1) was sequentially internally oxidised at 1273 and 1098 K to the Pd<sub>0.95</sub>Rh<sub>0.05</sub>/NiO and Pd/(NiO + Rh oxide) composites, respectively, and H isotherms were used to observe this. (1) was also internally oxidised at 1073 K in stages and the H isotherms showed three different plateau pressure regions. This proved that the Pt and Rh solutes are internally oxidised at different rates with the more stable oxide-forming solute (Ni) penetrating faster.

### First Principles Analysis of Hydrogen Chemisorption on Pd-Re Alloyed Overlayers and Alloyed Surfaces

V. PALLASSANA, M. NEUROCK, L. B. HANSEN and J. K. NØRSKOV, *J. Chem. Phys.*, 2000, 112, (12), 5435–5439

Gradient corrected periodic density functional theory slab calculations have been used to examine the chemisorption of atomic H on Pd-Re. Adsorption was examined at 33% surface coverage, where atomic H preferred the three-fold f.c.c. sites. The binding energy of atomic H varied by as much as 0.7 eV due to Pd-Re interactions. The computed adsorption energies were between –2.35 eV for Pd<sub>monolayer</sub>/Re(0001) and –3.05 eV for Pd<sub>33</sub>Re<sub>66</sub>/Pd(111).

### Optical Interband Spectra and Band Structure of Ru<sub>2</sub>Si<sub>3</sub> and Ru<sub>2</sub>Ge<sub>3</sub>

W. HENRION, M. REBIEN, A. G. BIRDWELL, V. N. ANTONOV and O. JEPSEN, *Thin Solid Films*, 2000, 364, (1, 2), 171–176

The optical spectra for Ru<sub>2</sub>Si<sub>3</sub> (1) and Ru<sub>2</sub>Ge<sub>3</sub> (2) exhibit semiconducting character with dominant interband features around 2 and 5 eV, and a relative minimum in the joint density of interband states at 3–4 eV. More pronounced structures were found for single crystalline samples of (1) and (2) than for solid phase crystallised thin films.

## CHEMICAL COMPOUNDS

### The First Metal Complexes of 1,4-Oxatellurane: Synthesis and Crystal Structure of Its Platinum(II) Complex

A. K. SINGH, M. KADARKARAIKAMY, S. HUSEBYE and K. W. TORNROOS, *J. Chem. Res. (S)*, 2000, (2), 64–65

*Trans*-[PtCl<sub>2</sub>L<sub>2</sub>] (L = 1,4-oxatellurane) (1) was synthesised and its structure was found to be centrosymmetric with Pt at the centre of symmetry. The Pt has square planar geometry. The Pt-Te bond length (2.5945 (3) Å) of (1) is similar to the average bond length of 2.582 Å found in *trans*-diiodobis(methylphenyltelluride)platinum(II). [PdCl<sub>2</sub>L<sub>2</sub>] did not give good quality crystals.

### Fluoroalkylated *N*-Heterocyclic Carbene Complexes of Palladium

L. XU, W. CHEN, J. F. BICKLEY, A. STEINER and J. XIAO, *J. Organomet. Chem.*, 2000, 598, (2), 409–416

Fluoroalkylated *N*-heterocyclic carbene complexes of Pd were synthesised from imidazolium salts and Pd(OAc)<sub>2</sub>. Analogous carbene complexes bearing long alkyl chains were also prepared. These carbene complexes were formed via an intermediate binuclear species, which has been isolated. Such complexes may have potential in homogeneous catalysis in *sc*-CO<sub>2</sub>.

### Synthesis, Characterization and Crystal Structure of a Series of Ruthenium Nitrosonaphthol Complexes

X.-X. LIU and W.-T. WONG, *Polyhedron*, 2000, 19, (1), 7–21

Substituted decarbonylation reactions conducted on five isomers of Ru nitrosonaphthols (1,2-naphthoquinone mono-oximes) affords a series of CO substituted complexes, including the centrosymmetric *trans*-, *trans*-[Ru{η<sup>2</sup>-N(O)C<sub>10</sub>H<sub>6</sub>O}<sub>2</sub>L<sub>2</sub>] (L = PBu<sub>3</sub>, 4-formylpyridine, 4-ethylpyridine, 4-dimethylaminopyridine) and the corresponding mono-CO-substituted complex. Properties were examined by electronic absorption spectra and electrochemical techniques.

## PHOTOCONVERSION

### Preparation and Optical Absorption Spectra of Au<sub>core</sub>Pt<sub>shell</sub> and Pt<sub>core</sub>Au<sub>shell</sub> Colloidal Nanoparticles in Aqueous Solution

A. HENGLEIN, *J. Phys. Chem. B*, 2000, 104, (10), 2201–2203  
Bimetallic core-shell type particles of Au-Pt (1) and Pt-Au (2) were prepared using H<sub>2</sub> reduction and radiolysis, respectively. Increasing Pt deposition in (1) damped the Au plasmon absorption band and moved it to shorter wavelengths until 510 nm (Au:Pt of 1:0.5). With further Pt deposition the intensity around 500 nm increases rapidly and the Au plasmon absorption disappears. (1) catalyses the reduction of Ag ions by H<sub>2</sub>. (2) exhibits increasing Pt absorption toward shorter wavelengths until a maximum at ~ 215 nm. As Au deposition increases, the Au plasmon absorption band appears with increasing intensity.

### Photoluminescence of [Rh<sup>III</sup>(phpy)<sub>2</sub>(CN)<sub>2</sub>]<sup>-</sup> (phpy<sup>-</sup> = *ortho*-Metalated 2-Phenylpyridine Anion)

H. KUNKELY and A. VOGLER, *Chem. Phys. Lett.*, 2000, 319, (5, 6), 486–488

Emission, excitation and absorption spectra of the title complex anion (1) in CH<sub>3</sub>CN, obtained by reaction of [Rh<sup>III</sup>(phpy)<sub>2</sub>Cl]<sub>2</sub> with CN<sup>-</sup>, were recorded by various techniques. (1) displays a blue-green photoluminescence at room temperature in solution (λ<sub>max</sub> = 460 and 490 nm, φ ≈ 0.006). This emission originates from a triplet state of the *ortho*-metalated phenylpyridine ligand.

### Preparation and Application of New Ruthenium(II) Polypyridyl Complexes as Sensitizers for Nanocrystalline TiO<sub>2</sub>

O. SCHWARZ, D. VAN LOYEN, S. JOCKUSCH, N. J. TURRO and H. DÜRR, *J. Photochem. Photobiol. A: Chem.*, 2000, 132, (1–2), 91–98

Ru(II) polypyridyls containing carboxylic and sulfonic 'anchor' groups were synthesised and studied as photosensitisers for nanocrystalline TiO<sub>2</sub> in Graetzel-type solar cells. Their performances were compared, relative to Ru(dcbpy)<sub>2</sub>(NCS)<sub>2</sub> (dcbpy = 2,2'-bipyridine-4,4'-dicarboxylic acid) (1), as an internal standard. Ru(dcphen)<sub>2</sub>(NCS)<sub>2</sub> (dcphen = 1,10-phenanthroline-4,7-dicarboxylic acid) showed a remarkable energy conversion efficiency of η = 62.3% compared to (1).

### Electrocatalysis in Photochemically Activated Electropolymerized Thin Films

J. A. MOSS, R. M. LEASURE and T. J. MEYER, *Inorg. Chem.*, 2000, 39, (6), 1052–1058

Poly-*cis*-[Ru(vbpy)<sub>2</sub>(py)](PF<sub>6</sub>)<sub>2</sub> (vbpy = 4-methyl-4'-vinyl-2,2'-bipyridine, py = pyridine) thin films on glassy C electrodes undergo photochemical ligand loss with HClO<sub>4</sub> to give poly-*cis*-[Ru(vbpy)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (1). The efficiency of ligand loss is greatly decreased compared to the efficiency in solution. In CVs of (1), Ru<sup>III/II</sup> and higher oxidation state Ru<sup>IV/III</sup>, Ru<sup>V/IV</sup> and Ru<sup>VI/V</sup> couples were observed. The redox chemistry of these films can be controlled by the electropolymerisation and external solution composition.

### Light-Induced Metastable States in Nitrosyl-Ruthenium Complexes Containing Ethylenediamine and Oxalate Ion Ligands

Y. MORIOKA, A. ISHIKAWA, H. TOMIZAWA and E.-I. MIKI, *J. Chem. Soc., Dalton Trans.*, 2000, (5), 781–786

Irradiation of *cis*-[Ru(Hox)(en)<sub>2</sub>NO]Cl<sub>2</sub>·EtOH, *trans*-[Ru(Hox)(en)<sub>2</sub>NO]Cl<sub>2</sub>, *cis*-K[Ru(ox)<sub>2</sub>(en)NO]·3H<sub>2</sub>O, *cis*-[Ru(Hox)(ox)(en)NO] and *cis*-K[Ru(ox)<sub>2</sub>(en)NO] in the solid state with blue-green light at 77 K produced a metastable state (1). Continued irradiation produced a photostationary state, as in Na nitroprusside. The population of the (1) molecules in the photostationary state depends on the λ, reaching a maximum at λ = 441.6 nm. The decay of (1) to the ground state occurs at temperatures considerably higher than that of the two metastable molecules of Na nitroprusside.

### Determination of Morpholine Fungicides Using the Tris(2,2'-bipyridine) Ruthenium(II) Chemiluminescence Reaction

J. M. GONZALEZ, G. M. GREENWAY, T. MCCREEDY and S. QIJUN, *Analyst*, 2000, 125, (4), 765–769

Chemiluminescence and electrogenerated chemiluminescence (ECL) based on the chemiluminescence reaction of Ru(bpy)<sub>3</sub><sup>2+</sup> (1) are sensitive and selective for the determination of dodemorph (2). In the chemiluminescence system, (1) was oxidised with Ce(IV). The flow rate, coil length and pH were optimised by a multivariate method. For ECL, (1) was oxidised at an Al working electrode. Good recoveries (96–100%) were achieved for (2) on cotton materials.

### Light Induced Production of Hydrogen from Water by Catalysis with Ruthenium Melanoidins

A. SERBAN and A. NISSENBAUM, *Int. J. Hydrogen Energy*, 2000, 25, (8), 733–737

H<sub>2</sub>O-insoluble Ru-melanoidin (1) was prepared by heating a solution of L-lysine, D-glucose, Na<sub>2</sub>CO<sub>3</sub> and RuCl<sub>3</sub>. (1) photocatalyses H<sub>2</sub> formation from H<sub>2</sub>O under light radiation ( $\lambda < 320$  nm), with EDTA as an electron donor and methyl viologen (2) as an electron relay. The bimolecular quenching constant for the quenching of melanoidin fluorescence by (2) was large ( $\sim 10^9$ ). The small Stern-Volmer constant ( $\sim 10$ ) indicated an inefficient electron transfer between the excited melanoidin and (2). (1) can be recycled.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Integration of Pt/Ru Electrode Structures by Metalorganic Chemical-Vapor Deposition on Poly-Si/SiO<sub>2</sub>/Si

E.-S. CHOI, J.-H. YANG, J.-B. PARK and S.-G. YOON, *J. Vac. Sci. Technol. B*, 2000, 18, (1), 262–266

Pt(130 nm)/Ru(80 nm) electrode structures were deposited on poly-Si by MOCVD. The Ru buffer layer (1) prevents the oxidation of poly-Si during annealing at 700°C in O<sub>2</sub> (760 Torr). The microstructure and conductivity of the Pt bottom electrode depended greatly on the annealing conditions of (1).

### Effects of Osmosis on Microstructure of Pd-Composite Membranes Synthesized by Electroless Plating Technique

R. S. SOULEIMANOVA, A. S. MUKASYAN and A. VARMA, *J. Membrane Sci.*, 2000, 166, (2), 249–257

Using osmosis during seeding and electroless plating of Pd thin films on porous Vycor glass allowed control of the metal grain size, microstructural uniformity and depth of metal penetration into the support. With osmosis, Pd could penetrate deeper into the porous substrate, forming an intermediate zone with gradually changing Pd-SiO<sub>2</sub> compositions. This enhanced thermal stability and mechanical properties that depend on adhesion between film and substrate.

### Polarization Behaviour and Lifetime of IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-SnO<sub>2</sub>/Ti Anodes in *p*-Phenolsulfonic Acid Solutions for Tin Plating

M. MORIMITSU, H. TAMURA, M. MATSUNAGA and R. OTOGAWA, *J. Appl. Electrochem.*, 2000, 30, (4), 511–514

The O overpotential of an IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-SnO<sub>2</sub>/Ti anode (1) in a solution containing *p*-phenolsulfonic acid (PSA) for Sn plating was a less positive potential than that of an IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode. Enhanced durability of (1) is due to the complete oxidation of PSA promoted by the SnO<sub>2</sub>, which results in the suppression of growth of organic film originating from PSA.

## APPARATUS AND TECHNIQUE

### A Thermoelectric Scanning Facility for the Study of Elemental Thermocouples

R. E. BENTLEY, *Meas. Sci. Technol.*, 2000, 11, (5), 538–546

The thermoelectric behaviour of Pt, Pd and Au, used in elemental thermocouples, was studied using a new scanning facility. Changes in Seebeck coefficient were measured along a 560 mm length of each of three wires, relative to a fourth, by moving them through a 50 mm long, e.m.f.-producing zone into a uniform-temperature region at 250°C. E.m.f. measurements were made to 10 nV ( $\sim 1$  mK). Changes of  $\sim 10$  ppm could be detected in Seebeck coefficient.

### Silicon-Carbide MOS Capacitors with Laser-Ablated Pt Gate as Combustible Gas Sensors

A. SAMMAN, S. GEBREMARIAM, L. RIMAI, X. ZHANG, J. HANGAS and G. W. AUNER, *Sens. Actuators B, Chem.*, 2000, 63, (1–2), 91–102

SiC MOS capacitors were prepared with Pt gates deposited by pulsed laser ablation. The response of their complex admittance, between 62.5 kHz and 1 MHz, to propane, propylene and CO was similar to that for capacitors with sputtered Pt gates. However, contrary to the sputtered Pt, the laser-ablated Pt showed no adhesion problems to the SiO<sub>2</sub>, even for prolonged operation at high temperatures.

## HETEROGENEOUS CATALYSIS

### Modelling of the Metallic Phases of Different Pt-Rh/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> Catalysts: Influence of the Rhodium Loading and Nature of the Metallic Precursors

L. PIRAULT-ROY, M. GUÉRIN, F. MAIRE, P. MARÉCOT and J. BARBIER, *Appl. Catal. A: Gen.*, 2000, 199, (1), 109–122

The activities for propane-propene oxidation under lean conditions using three-way Pt-Rh/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> (1) catalyst were found to depend on the preparative method. (1) was prepared either by coimpregnation (CI) of the metallic salts or by successive impregnations (SI) with an intermediary reducing treatment. The formation of clusters of inactive Pt-Rh alloys of a rather homogeneous composition was suggested for (CI) catalysts, while active bimetallic catalysts obtained by (SI) were modelled by Pt and Rh clusters more or less mixed together.

## Enhancement of the Catalytic Oxidation of Hydrogen-Lean Chlorinated VOCs in the Presence of Hydrogen-Supplying Compounds

J. R. GONZÁLEZ-VELASCO, A. ARANZABAL, R. LÓPEZ-FONSECA, R. FERRET and J. A. GONZÁLEZ-MARCOS, *Appl. Catal. B: Environ.*, 2000, 24, (1), 33–43

The complete catalytic oxidation of trichloroethylene (TCE) admixed with H<sub>2</sub>O, hexane and toluene, over 0.42 wt.% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (1) and 0.44 wt.% Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (2) was carried out under O<sub>2</sub>-rich conditions. Over (1), H<sub>2</sub>O did not alter catalytic activity. Over (2), H<sub>2</sub>O enhanced TCE oxidation at low temperatures (< 400°C) but inhibited it at higher temperatures (> 400°C). TCE oxidation occurred faster in the presence of hexane and toluene over both (1) and (2).

## Oxidation and Reduction Effects of Propane–Oxygen on Pd-Chlorine/Alumina Catalysts

M. SCHMAL, D. A. G. ARANDA, F. B. NORONHA, A. L. GUIMARÃES and R. S. MONTEIRO, *Catal. Lett.*, 2000, 64, (2–4), 163–169

Pd/Al<sub>2</sub>O<sub>3</sub> (1) was prepared by incipient-wetness impregnation of Al<sub>2</sub>O<sub>3</sub> with a HCl solution of PdCl<sub>2</sub>. Temperature programmed surface reaction measurements for propane oxidation on the Pd surface under excess hydrocarbon showed three reactions: complete oxidation, steam reforming and propane hydrogenolysis. Pd<sup>2+</sup> species were shown to prevail during the propane reaction and these particles are more active for combustion. CO species adsorbed on Pd<sup>0</sup> were noted in all samples after reaction. The Pd<sup>0</sup>:Pd<sup>2+</sup> surface ratio determined the propane oxidation activity.

## Hydrogenolysis of CFC-12 (CF<sub>2</sub>Cl<sub>2</sub>) over Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Pretreated with HCFC-22 (CHF<sub>2</sub>Cl)

B. S. AHN, S. G. JEON, H. LEE, K. Y. PARK and Y. G. SHUL, *Appl. Catal. A: Gen.*, 2000, 193, (1, 2), 87–93

Hydrogenolysis of CF<sub>2</sub>Cl<sub>2</sub> in the gas phase at 250°C was carried out over 3 wt.% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (1). Pretreatment of (1) with CHF<sub>2</sub>Cl significantly improved the catalytic activity and the catalyst lifetime compared to conventional reduction. XRD and XPS characterisation identified that CHF<sub>2</sub>Cl pretreatment had induced Pd carbide formation. TEM showed that CHF<sub>2</sub>Cl had also greatly reduced sintering of Pd. Pd carbide is also assumed to have increased partial hydrodehalogenation from CF<sub>2</sub>Cl<sub>2</sub> to CH<sub>2</sub>F<sub>2</sub>.

## Catalytic Reduction in Subcritical Water

J. M. JENNINGS, T. A. BRYSON and J. M. GIBSON, *Green Chem.*, 2000, 2, (2), 87–88

Catalytic hydrogenation of olefins and acetylenes was achieved in the presence of 10% Pd/C in subcritical H<sub>2</sub>O, using Na formate (1) as the H source. The solubility of the unsaturated organic materials and use of H<sub>2</sub>O at below the critical point (374°C and 218 atm) allows the reactions to proceed. (1) also acts as a weak base or buffer. The complete separation of the organic and H<sub>2</sub>O phases on cooling the system post-reaction allows product recovery and purification.

## Nanotechnology and Model Catalysis: The Use of Photolithography for Creating Active Surfaces

R. PRINS, M. SCHILDENBERGER, Y. C. BONETTI and J. GOBRECHT, *Chimia*, 2000, 54, (1/2), 63–65

Model Pd catalysts, “nanotowers” and “nanopits”, containing 10<sup>9</sup>–10<sup>10</sup> active Pd sites on an otherwise flat SiO<sub>2</sub> surface on oxidised 4-inch wafers were produced using lithographic processes. These arrays have great potential because of the unique combination of uniformity, stability and large Pd surface area.

## Catalytic Activity of Ir for NO-CO Reaction in the Presence of SO<sub>2</sub> and Excess Oxygen

M. OGURA, A. KAWAMURA, M. MATSUKATA and E. KIKUCHI, *Chem. Lett. Jpn.*, 2000, (2), 146–147

Ir/amorphous SiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or silicalite catalysts were investigated for NO reduction with CO in the presence of SO<sub>2</sub> and excess O<sub>2</sub>. A promoting effect by the support on the catalytic activity of Ir was observed, especially in the presence of SO<sub>2</sub>. Ir/silicalite (1) catalysed NO reduction with CO selectively in an atmosphere containing 1–10% O<sub>2</sub> at 300–500°C. The catalytic activity was hardly influenced by 150 ppm SO<sub>2</sub>. NO conversion increased with increasing O<sub>2</sub> concentration at lower temperatures, and 42% NO was selectively reduced with (1) by CO at 365°C in the presence of 10% O<sub>2</sub> and 150 ppm SO<sub>2</sub>.

## HOMOGENEOUS CATALYSIS

### Heck Reactions of Iodobenzene and Methyl Acrylate with Conventional Supported Palladium Catalysts in the Presence of Organic and/or Inorganic Bases without Ligands

F. ZHAO, B. M. BHANAGE, M. SHIRAI and M. ARAI, *Chem. Eur. J.*, 2000, 6, (5), 843–848

The vinylation of iodobenzene with methyl acrylate was investigated on Pd/SiO<sub>2</sub>, Pd/C or Pd/Mg-containing smectite-like material in *N*-methylpyrrolidone in the presence of triethylamine and/or Na<sub>2</sub>CO<sub>3</sub>. The reaction was performed in air without any solubilising or activating ligands. Pd leached into the solvent and the Pd dissolved species then catalysed the Heck reaction. The use of mixed organic and inorganic bases promotes Pd redeposition onto the support, and enhances the reaction rate. The catalyst is reusable.

### A New Route to Fused Aromatic Compounds by Using a Palladium-Catalyzed Alkylation – Alkenylation Sequence

M. LAUTENS and S. PIGUEL, *Angew. Chem. Int. Ed.*, 2000, 39, (6), 1045–1046

Using Pd(OAc)<sub>2</sub>, tri-2-furylphosphane, norbornene, M<sub>2</sub>CO<sub>3</sub> (M = K or Cs) and MeCN, the Pd-catalysed reaction of *ortho*-substituted aryl iodides (1) with ethyl (*E*)-6-bromohex-2-enoate and ethyl (*E*)-7-bromohex-2-enoate gave carbocycles with 6- and 7-membered rings, respectively, in moderate to excellent yields. The yield of the reaction was strongly influenced by the *ortho*-alkyl substituent of (1).

## A Stable, Conspicuously Active, Water-Soluble Pd Catalyst for the Alternating Copolymerization of Ethene and CO in Water

G. VERSPUI, F. SCHANSSEMA and R. A. SHELDON, *Angew. Chem. Int. Ed.*, 2000, 39, (4), 804–806

A new H<sub>2</sub>O-soluble catalyst, Pd with tetra-sulfonated diphosphane (1,3-C<sub>3</sub>H<sub>6</sub>[P(C<sub>6</sub>H<sub>3</sub>-2-OMe-5-SO<sub>3</sub>Na)<sub>2</sub>]<sub>2</sub>) (1), was synthesised in high purity and low yield. (1) catalyses the alternating copolymerisation of ethene and CO in H<sub>2</sub>O. Alternating copolymers with high molecular weights are formed. (1) did not require a Brønsted acid cocatalyst for high stability and activity. (1) can be recovered by filtering off the product.

## Synthesis of Linear and Branched Polyketones from the Rh Complex Catalyzed Living Alternating Copolymerization of (4-Alkylphenyl)allene with CO

K. OSAKADA, Y. TAKENAKA, J.-C. CHOI, I. YAMAGUCHI and T. YAMAMOTO, *J. Polym. Sci. A: Polym. Chem.*, 2000, 38, (9), 1505–1511

Copolymerisation of (4-hexylphenyl)allene (1) and of (4-dodecylphenyl)allene with CO catalysed by Rh( $\eta^3$ -CH(Ar')<sub>2</sub>C{C(=CHAr')CH<sub>2</sub>C(=CHAr')CH<sub>2</sub>CH<sub>2</sub>CH=CHAr'}CH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub> (Ar' = C<sub>6</sub>H<sub>4</sub>OMe-*p*) was performed. Polyketones from (1) and CO, with molecular weights similar to those calculated from the monomer:initiator ratios, up to a molecular weight of 45,000, were produced, indicating living polymerisation. A mixture of (4-methylphenyl)allene and smaller amounts of bis(allenyl)benzene under CO gave a crosslinked polyketone.

## Stereoselectivity in the Rhodium(II) Acetate Catalysed Cyclopropanations of 2-Diazo-1-indanone with Styrenes

W. BAUTA, J. DODD, J. BULLINGTON, D. GAUTHIER, G. LEO and P. McDONNELL, *Tetrahedron Lett.*, 2000, 41, (10), 1491–1494

Rh<sub>2</sub>(OAc)<sub>4</sub> catalysed cyclopropanation reactions of 2-diazo-1-indanone with substituted styrenes were investigated. A cyclopropane diastereomer bearing a *trans* relationship between the carbonyl and the aryl ring was in all cases the predominant isomer and the ratio of stereoisomers was almost constant over the range of styrene substituents evaluated.

## Low-Valent Ruthenium and Iridium Hydride Complexes as Alternatives to Lewis Acid and Base Catalysts

S.-I. MURAHASHI and H. TAKAYA, *Acc. Chem. Res.*, 2000, 33, (4), 225–233

Nitriles can be activated by low valent Ru complexes and Ir complexes, acting as Lewis acid and base catalysts. After activation by these catalysts, the nitriles undergo reactions with either nucleophiles or electrophiles under neutral conditions. Hydration of nitriles, esterification of nitriles with alcohols, and amidation of nitriles with amines were all achieved together with NH<sub>3</sub> formation. The complexes provide a novel way to catalytic C–C bond formation.

## Dearomatization of Naphthalene: Novel Stereoselective Cyclization Reactions Promoted by Osmium(II)

M. D. WINEMILLER and W. D. HARMAN, *J. Org. Chem.*, 2000, 65, (5), 1249–1256

A series of Michael acceptors were combined with the Os(II)  $\eta^2$ -naphthalene complex (from the coordination of naphthalene with [Os(NH<sub>3</sub>)<sub>5</sub>]<sup>2+</sup>) (1) to form stable 1*H*-naphthalenium species. Under acidic conditions, these complexes undergo ring closure at C2 to form the phenanthrene core. In contrast, the corresponding 1-methylnaphthalene complex upon addition of methyl vinyl ketone (MVK) at C8 undergoes ring closure at C5 to form a bridged tricyclic complex. Michael addition of MVK to (1) followed by deprotonation, an inter-ring linkage isomerisation and ring closure gave a 9-methylphenalene complex.

## Catalytic Hydrogenation of Acrylonitrile-Butadiene Copolymers by a Series of Osmium Complexes

T.-F. MAO and G. L. REMPEL, *J. Mol. Catal. A: Chem.*, 2000, 153, (1–2), 63–73

The activity of Os phosphine complexes (1) as catalysts for the hydrogenation of nitrile-butadiene copolymers was investigated under 3.42 MPa of H<sub>2</sub> and at 130°C in monochlorobenzene. Activity of (1) was: class I (bulky monophosphines with Tolman's cone angle  $\geq 160^\circ$ ) OsHCl(CO)(O<sub>2</sub>)(PR<sub>3</sub>)<sub>2</sub> (PR<sub>3</sub> = P<sup>*i*</sup>Pr<sub>3</sub>, PCy<sub>3</sub>, PCy<sub>2</sub>Ph) > class II (small monophosphines) OsHCl(CO)(PR<sub>3</sub>)<sub>2</sub> (PR<sub>3</sub> = PPh<sub>3</sub>, P(*m*-C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>) > class III (diphosphines) OsHCl(CO)(PPh<sub>3</sub>)(dppp) (dppp = Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub>).

## Synthesis of Poly(silyl ethers) by Ru-Catalyzed Hydrosilylation

J. M. MABRY, J. K. PAULASAARI and W. P. WEBER, *Polymer*, 2000, 41, (12), 4423–4428

Dihydridocarbonyltris(triphenylphosphine)Ru, activated with a stoichiometric amount of styrene, catalysed the hydrosilylation polymerisation of dimethylsilyloxyaryl ketones or aldehydes and the copolymerisation of aromatic  $\alpha,\omega$ -diketones and oligo- $\alpha,\omega$ -dihydridodimethylsiloxanes to poly(silyl ethers). The Ru catalysed addition of Si–H bonds across C=O bonds to form CH–O–Si is the key to polymerisation.

## FUEL CELLS

### EXAFS of Carbon Monoxide Oxidation on Supported Pt Fuel Cell Electrocatalysts

S. MANIGUET, R. J. MATHEW and A. E. RUSSELL, *J. Phys. Chem. B*, 2000, 104, (9), 1998–2004

The potential dependence of the EXAFS obtained at the Pt L<sub>III</sub> absorption edge for Pt/C electrocatalyst exposed to CO is reported. Adsorbed CO was observed with a Pt–C distance of 1.85 Å at potentials < 0.5 V vs. RHE. Increasing the potential > 0.5 V resulted first in the removal of the adsorbed CO and at more positive potentials, such as 1.05 V, in the formation of an oxide layer.

## Application of Pd-Based Electrodes as Hydrogen Diffusion Anodes in Alkaline Fuel Cells

P. L. CABOT, E. GUEZALA, J. C. CALPE, M. T. GARCÍA and J. CASADO, *J. Electrochem. Soc.*, 2000, 147, (1), 43–49

The anode current and power densities of AFCs using Pd-based H<sub>2</sub> diffusion anodes were measured at 25 and 50°C. A treated Pd foil (25 μm thick) and a Pt-catalysed C-PTFE electrode were employed as anode and cathode, respectively. There was a strong tendency for the Pd foil to cease during fuel cell operation. A PdO film produced on the Pd foil by heating in a furnace was a good catalyst for the overall anodic process. The highest cell parameters were obtained when Pt black was electrodeposited on Pd black.

## An Ultrasafe Hydrogen Generator: Aqueous, Alkaline Borohydride Solutions and Ru Catalyst

S. C. AMENDOLA, S. L. SHARP-GOLDMAN, M. S. JANJUA, M. T. KELLY, P. J. PETILLO and M. BINDER, *J. Power Sources*, 2000, 85, (2), 186–189

High purity H<sub>2</sub> gas for PEMFCs can be generated from stable H<sub>2</sub>O solutions of NaBH<sub>4</sub> and Ru/anion exchange resin catalyst (1). When NaBH<sub>4</sub> solution comes in contact with (1), it spontaneously hydrolyses to form H<sub>2</sub> and Na borate. High H<sub>2</sub> generation rates are achieved. When H<sub>2</sub> is no longer required, (1) is removed from the solution and H<sub>2</sub> generation stops.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Orientation Control in PZT/Pt/TiN Multilayers with Various Si and SiO<sub>2</sub> Underlayers for High Performance Ferroelectric Memories

K. KUSHIDA-ABDELGHAFAR, K. TORII, T. MINE, T. KACHI and Y. FUJISAKI, *J. Vac. Sci. Technol. B*, 2000, 18, (1), 231–236

Preferred orientation in PZT/Pt/TiN/Si and SiO<sub>2</sub> multilayers was investigated to control the crystalline quality of PZT films which affects capacitor characteristics. The (111) orientation, which is closely related to spontaneous polarisation, was achieved when PZT film was grown on highly (111) orientated Pt film. The degree of Pt(111) orientation was dependent on the crystallinity of the underlying TiN barrier metal. The use of an amorphous Si buffer layer can improve the TiN crystallinity of the whole capacitor.

### Preparation of Pt/Ru Bilayers and Their Application to the Capacitor of Memory Devices

B. S. LEE and Y. C. CHOI, *Jpn. J. Appl. Phys., Part 1*, 2000, 39, (1), 222–226

Pt/BST/Pt, Pt/BST/RuO<sub>2</sub> and Pt/BST/Pt/Ru (BST = (Ba,Sr)TiO<sub>3</sub>) capacitors were fabricated and studied. The microstructures of BST films were affected by those of the bottom electrodes, and had an effect on the electrical properties of the capacitors. Dielectric constant and leakage current density of the capacitors with Pt/Ru bottom electrodes are analogous to those with Pt bottom electrodes but better than those with RuO<sub>2</sub> bottom electrodes.

## Molybdenum-Ruthenium/Beryllium Multilayer Coatings

S. BAJT, *J. Vac. Sci. Technol. A*, 2000, 18, (2), 557–559

A new Be-based multilayer system (1) consisting of polycrystalline Be and amorphous MoRu layers has been developed. Layers were deposited using a magnetron sputtering technique. (1) has a reflectivity as high as 69.3% at a wavelength of 11.4 nm (50 bilayers giving a bandwidth of 0.35 nm), near-zero in intrinsic stress, and excellent smoothing properties.

## MEDICAL USES

### Kinetics and Mechanism for Reduction of the Anticancer Prodrug *trans,trans,trans*-

[PtCl<sub>2</sub>(OH)<sub>2</sub>(*c*-C<sub>6</sub>H<sub>11</sub>NH<sub>2</sub>)(NH<sub>3</sub>)] (JM335) by Thiols

K. LEMMA, T. SHI and L. I. ELDING, *Inorg. Chem.*, 2000, 39, (8), 1728–1734

The reduction of JM335 (1) by L-cysteine, DL-penicillamine, DL-homocysteine, N-acetyl-L-cysteine, 2-mercaptopropanoic acid, 2-mercaptosuccinic acid and glutathione was fairly rapid in moderately alkaline aqueous perchlorate. The half-life for reduction of (1) by 6 mM glutathione (40-fold excess) at physiologically relevant conditions of pH 7.30 and 37°C was 23 s. (1) is likely to undergo *in vivo* reduction by intracellular reducing agents prior to binding to DNA.

### Chiral and Achiral Platinum(II) Complexes for Potential Use as Chemotherapeutic Agents:

Crystal and Molecular Structures of *cis*-[Pt(L')<sub>2</sub>] and [Pt(L')Cl(MPSO)] [HL' = *N,N*-Diethyl-*N'*-benzoylthiourea]

C. SACHT, M. S. DATT, S. OTTO and A. ROODT, *J. Chem. Soc., Dalton Trans.*, 2000, (5), 727–733

Complexes of [Pt(acylthioureato)Cl(RR'SO)] were synthesised by reaction of [PtCl<sub>2</sub>(RR'SO)]<sub>2</sub> with acylthiourea ligands in the presence of Na acetate. [Pt(acylthioureato)Cl(DMSO)] with thiourea ligands: *N,N*-diethyl-*N'*-(*m*-nitrobenzoyl)-, *N*-morpholino-*N'*-(*m*-nitrobenzoyl)- and *N*-morpholino-*N'*-(*m*-methoxybenzoyl)- showed a notable antiproliferative effect on a HeLa cancer cell line.

### New Ruthenium(III) Complexes Containing Tetradentate Schiff Bases and Their Antibacterial Activity

T. D. THANGADURAI and K. NATARAJAN, *Transition Met. Chem.*, 2000, 25, (3), 347–351

Complexes [RuX(EPh<sub>3</sub>)(LL')] (X = Cl, Br; E = P, As; LL' = acacetyl, dbm-tet, dbm-*o*-ph) (1) were prepared by reaction of [RuCl<sub>3</sub>(PPh<sub>3</sub>)<sub>3</sub>], [RuCl<sub>3</sub>(AsPh<sub>3</sub>)<sub>3</sub>], [RuBr<sub>3</sub>(AsPh<sub>3</sub>)<sub>3</sub>] and [RuBr<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>(MeOH)] with the Schiff bases bis(acetylacetonate)tetramethylenediamine (H<sub>2</sub>acacetyl), bis(dibenzoylmethane)tetramethylenediamine (H<sub>2</sub>dbm-tet) and bis(dibenzoylmethane)-*o*-phenylenediamine (H<sub>2</sub>dbm-*o*-ph). (1) showed higher activity against bacteria *Salmonella aureus* and *Salmonella typhi* than standard bacteriocides.