

# ABSTRACTS

of current literature on the platinum metals and their alloys

## PROPERTIES

### Sputtering Behaviour of Stainless Steel during Pt Ion Implantation

L. CLAPHAM, J. L. WHITTON and M. C. RIDGWAY, *Mater. Lett.*, 1993, 16, (2, 3), 139–141

Studies of the sputtering and saturation behaviour of 316 stainless steel targets bombarded with 1500 keV Pt ions were performed. Progressively higher doses of Pt were implanted into stainless steel and the retained dose determined in order to produce a saturation curve. The sputter yield of Pt in stainless steel lies between 8 and 9, in contrast to predicted  $\approx 15$ .

### Microstructural Properties of Pt-Doped $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ High- $T_c$ Superconductor Prepared by Melting Method

J.-H. PARK, H.-W. KIM and J.-T. SONG, *J. Mater. Sci. Mater. Electron.*, 1993, 4, (1), 77–82

The effect of Pt additions on the superconducting properties of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (123) and the formation mechanism of the fine dispersion of  $\text{Y}_2\text{BaCuO}_5$  (211) particles in the (123) superconductor, prepared by a melting method, were studied. In 1 wt.% Pt-added samples  $\sim 1\text{--}2\ \mu\text{m}$  211 particles were finely dispersed in the 123 matrix. The critical temperature of Pt-doped samples was 91.5 K and the transport critical current,  $J_c$ , of Pt-doped samples was  $> 10^4\ \text{A/cm}^2$ .

### Controlled Surface Damage Using a Scanning Tunnelling Microscope on Platinum and Platinum-Carbon Films and the *in-situ* Correction of Tip Defects

C. J. ROBERTS, M. C. DAVIES, D. E. JACKSON and S. J. B. TENDLER, *Ultramicroscopy*, 1993, 48, (3), 265–272

Scanning tunnelling microscopy has been used to alter the surface morphology of Pt and Pt-C films to create stable features by employing tunnelling biases  $> \pm 2.9\text{--}3.1\ \text{V}$  and  $\pm 3.2\text{--}3.4\ \text{V}$ , respectively. Surface trenches can be created by moving a tip which is highly biased. For Pt-C material can be deposited.

### Heterogeneous Systems Based on Precious Metal Powders and Polymers

R. KUŽEL, J. KUBÁT, I. KRŮVKA, J. PROKEŠ, O. STEFAN and C. KLASON, *Mater. Sci. Eng.*, 1993, B17, (1–3), 190–195

New types of heterogeneous systems based on polyethylene or polystyrene matrices containing Pd, Au and Ag powder, in the form of spheres, or containing  $\text{RuO}_2$  have been developed. The materials were characterised by resistance measurements as a function of powder content and dependence of the impedance and phase angle or capacitance on the powder content at various frequencies and temperatures.

### Electromigration-Resistant Cu-Pd Alloy Films

C. W. PARK and R. W. VOOK, *Thin Solid Films*, 1993, 226, (2), 238–247

High resistance to electromigration damage was obtained by alloying Cu with a small amount of Pd with Cu-Pd alloy films being deposited on oxidised Si wafers by vacuum evaporation. The activation energies of Cu, Cu–0.5 wt.% Pd, Cu–1.0 wt.% Pd and Cu–1.6 wt.% Pd films were 0.79, 1.01, 1.26 and 1.15 eV, respectively. X-ray energy spectroscopy showed that hillocks on the Cu-Pd alloy films had a lower Pd concentration than hillock-free areas.

### Effect of 3d-Elements on Magnetic Susceptibility of Ordering Cu-Pd Alloy

I. I. PIRATINSKAYA, E. A. BALINA, YU. A. VERESHCHAGIN and L. P. ZELENIN, *Fiz. Metal. Metalloved.*, 1993, 75, (1), 71–77

Studies of the magnetic susceptibility of  $\text{Cu}_{40-x}\text{Pd}_{40}\text{Me}_x$ , where  $\text{Me} = \text{Cr}$  or  $\text{Mn}$ ;  $\text{Cu}_{35-x}\text{Pd}_{45}\text{Me}_x$ , where  $\text{Me} = \text{Co}$  or  $\text{Fe}$ ,  $x = 1\text{--}3\ \text{at.}\%$ ; and  $\text{Cu}_{50}\text{Pd}_{35}\text{Ni}_x$  alloys were performed at 300–1200 K. Pd-based alloys containing Cu showed a widening of the stable region of the ordered B2-phase, as well as the formation of a region near to order in the atomically-reordered structure. The interaction between the magneto-active atoms changed the ordering from diamagnetic to para- and ferromagnetic.

### Isothermal Section of the Palladium-Titanium-Cobalt System at 800°C

D. M. GERGAULOVA, M. V. RAEVSKAYA and A. L. TATARKINA, *Vestn. Moskov. Univ., Ser. Khim.*, 1992, 33, (4), 369–372

Phase equilibrium was studied by various physico-chemical techniques and an isothermal section of Pd-Ti-Co at 800°C was constructed. Solubility of binary intermetallic compounds in the Pd-Ti-Co system was established. A ternary phase was discovered on the boundary of  $\text{TiCo}_3$  and  $\text{TiPd}_3$ .

### Interaction of Intermetallic Compounds $\text{Zr}_2\text{Pd}$ , $\text{Hf}_2\text{Pd}$ and $\text{Hf}_2\text{Cu}$ with Hydrogen under Pressure up to 2000 atm

S. N. KLYAMKIN, K. N. SEMENENKO and I. A. KINAS, *Vestn. Mosk. Univ., Ser. Khim.*, 1993, 34, (1), 67–74

High gas pressure studies of interaction of the intermetallic compounds  $\text{Zr}_2\text{Pd}$ ,  $\text{Hf}_2\text{Pd}$  and  $\text{Hf}_2\text{Cu}$  which crystallise with the  $\text{MoSi}_2$  type structure, with  $\text{H}_2$  were performed under  $\leq 2000\ \text{atm}$ . Isotherms of absorption and desorption of H at 293 K were defined. Hydride phases  $\text{A}_2\text{BH}_3$  and  $\text{A}_2\text{BH}_{3.5-6}$ , where A is Zr or Hf, and B is Pd, were formed under  $\text{H}_2$  pressure, with the trihydride phase retaining the tetragonal structure of the initial intermetallic compounds.

### X-Ray Photoelectron Spectroscopy Studies of Fired Palladium Electrode Ink Materials

N. M. D. BROWN, J. A. HEWITT and B. J. MEENAN, *Surf. Interface Anal.*, 1993, 20, (3), 215–220

Pd inks for use in multilayer ceramic capacitors were studied by XPS after application to Ba titanate dielectric substrates as a function of both firing temperature and firing atmosphere. Several states, Pd metal, PdO<sub>ads</sub>, PdO and Pd in one or more higher oxidation states, were found. The ink fired at 1350°C in air had a sub-surface of metallic Pd although the original surface was PdO, as required for electrode layer conduction.

### In situ Strain Measurements during the Formation of Palladium Silicide Films

P. P. BUAUD, F. M. D'HEURLE, S. CHEVACHAROENKUL and E. A. IRENE, *J. Vac. Sci. Technol. B*, 1993, 11, (2), 304–310

The evolution of strain in the Pd-Si system during the growth of Pd<sub>3</sub>Si thin films on Si(100) has been examined by a double optical beam reflection technique. The reaction to form Pd<sub>3</sub>Si gives a compressive intrinsic surface film stress. Film growth is governed by the motion of Pd atoms, which are the predominant moving species until the film growth slows because of the thickening of Pd<sub>3</sub>Si. Whereupon relaxation occurs requiring both Pd and Si atom motion. An oxide layer formed at 225°C is very thin and cannot influence the evolution of the silicide stresses. A value of  $3 \times 10^{-14}$  cm<sup>2</sup>/s was found for the diffusion coefficient of Pd in Pd<sub>3</sub>Si at 235°C.

### Morphological and Magnetic Properties of Ru, Os and Ir-Substituted Fe<sub>3</sub>N

D. ANDRIAMANDROSO, S. MATAR, G. DEMAZEAU and L. FOURNÈS, *IEEE Trans. Magn.*, 1993, 29, (1), Pt. 1, 2–6

Fe<sub>3</sub>N substituted with Ir, Os and Ru by co-precipitating their mixed hydroxides with Fe, have been studied for use in magnetic recording materials. Saturation magnetisation and coercive fields were measured and Curie temperature measurements were taken. These substitutions lead to very fine particles with superparamagnetic behaviour.

### The High-Temperature Electron Emission and Vaporization of Tungsten-Osmium Alloys

R. N. WALL, D. L. JACOBSON and D. R. BOSCH, *Metall. Trans. A*, 1993, 24, (4), 951–958

The enhanced work functions of three arc-melted and one sintered W-Os alloys containing 4.76–13.05 wt.% Os were examined at their polycrystalline surfaces at 1700–2800 K. The work function of the sintered and arc-melted W-5% Os alloys did not vary with increase in temperature, while the arc-melted W-9% Os and W-13% Os both exhibited a constant work function. The highest observed work function of 4.92 eV was obtained at 2100 and 2200 K from the W-13% Os alloy. The W-13% Os alloy had the highest work functions (4.85–4.92 eV) over the entire temperature range.

### The Structural and Electronic Properties of the Ru(V) Perovskites Ba<sub>2</sub>LaRu<sub>0.5</sub>Sb<sub>0.5</sub>O<sub>6</sub> and Ba<sub>2</sub>TaRu<sub>0.5</sub>Na<sub>0.5</sub>O<sub>6</sub>

S. A. ALMAER, P. D. BATTLE, P. LIGHTFOOT, R. S. MELLEEN and A. V. POWELL, *J. Solid State Chem.*, 1993, 102, (2), 375–381

Studies of the magnetic properties of Ru(V) when present in low concentrations in a mixed metal oxide were performed on Ba<sub>2</sub>LaRu<sub>0.5</sub>Sb<sub>0.5</sub>O<sub>6</sub> (1) and Ba<sub>2</sub>TaRu<sub>0.5</sub>Na<sub>0.5</sub>O<sub>6</sub> (2). The effective magnetic moment, 3.44 μ<sub>B</sub>, deduced from the high-temperature magnetic susceptibility of (2) was in the range expected for a localised-electron 4d<sup>1</sup>:<sup>4</sup>A<sub>1g</sub> system with Ru(V) cations lying within the localised electron regime, and was 3.78 μ<sub>B</sub> for Ru(V) in (1).

### The Observation of Resistance Oscillations in Metals at High Magnetic Fields Using a SQUID

I. R. WALKER, *J. Low Temp. Phys.*, 1993, 90, (3/4), 205–241

A SQUID has been used as the amplifying element to detect electromagnetic energy in heavy fermion compound CeRu<sub>2</sub>Si<sub>2</sub> placed within a dilution refrigerator probe at 0.02 K in magnetic fields of 13.7 T. CeRu<sub>2</sub>Si<sub>2</sub> undergoes a metamagnetic transition at a field of 8 T. Oscillations of 10<sup>9</sup> Ω were detected against a background resistance of ~10<sup>5</sup> Ω, using excitation currents of around 10<sup>-2</sup> A.

## CHEMICAL COMPOUNDS

### Synthesis and Carbonylation of [Pd(Me)(OMe){(S,S)-bdpp}][{(S,S)-bdpp} = (2S,4S)-2,4-bis(diphenylphosphino)pentane]

I. TÓTH and C. J. ELSEVIER, *J. Chem. Soc., Chem. Commun.*, 1993, (6), 529–531

Synthesis of the title compound by NaOMe metathesis with [Pd(Me)(Cl){(S,S)-bdpp}] is reported along with the low temperature carbonylation of the title compound. The elimination of methyl acetate from the new carbonylation product [Pd(Me)(CO<sub>2</sub>Me){(S,S)-bdpp}] proceeded readily even at -50°C. The methyl(methoxycarbonyl) compound readily eliminated MeCO<sub>2</sub>Me.

### Synthesis of a Rhodium Methylthiolate and Insertion of CS<sub>2</sub> into the Rh-SCH<sub>3</sub> Bond. Structure of the Thioxanthate [(pp<sub>3</sub>)RhSC(S)SCH<sub>3</sub>] [pp<sub>3</sub> = Tris(2-(Diphenylphosphino)ethyl)phosphine]

M. DI VAIRA, D. ROVAI and P. STOPPIONI, *Polyhedron*, 1993, 12, (1), 13–17

The isolation and structure determination of a mononuclear Rh(I) methylthiolate stabilised by the pp<sub>3</sub> ligand is reported. The reaction of the (pp<sub>3</sub>)Rh<sup>I</sup> fragment with NaSCH<sub>3</sub> yielded the methylthiolate derivative [(pp<sub>3</sub>)RhSCH<sub>3</sub>]. The S atom of the compound was attacked by the electrophile CF<sub>3</sub>SO<sub>2</sub>CH<sub>3</sub> to yield the stable dimethylsulphide complex [(pp<sub>3</sub>)RhS(CH<sub>3</sub>)<sub>2</sub>]CF<sub>3</sub>SO<sub>2</sub>.

## Synthesis of Fullerene-Rhodium Nanocomposites via Aerosol Decomposition

A. S. GURAV, Z. DUAN, L. WANG, M. J. HAMPDEN-SMITH and T. T. KODAS, *Chem. Mater.*, 1993, 5, (2), 214–216  
Highly dispersed (20–100 nm) powders consisting of nanophase fullerenes and their nanocomposites with Rh were generated by aerosol decomposition. Solutions of mixed fullerene extract ( $C_{60}$ ,  $C_{70}$ ) and [(1,5-COD)RhCl]<sub>2</sub> (1) in toluene were atomised and passed through a hot-wall reactor in a N<sub>2</sub> carrier gas where toluene evaporation and thermal decomposition of (1) to form Rh occurred. Nanocomposite particles were formed at a reactor temperature of 550°C which was sufficiently low to avoid C<sub>60</sub> and Rh grain growth in each particle but sufficiently high to thermally decompose (1).

## Fluxional Ligand Migrations in Triosmium Clusters Containing 2-Pyridylphosphines

A. J. DEEMING and M. B. SMITH, *J. Chem. Soc., Chem. Commun.*, 1993, (10), 844–846

X-ray structural studies of the cluster [Os<sub>3</sub>(CO)<sub>10</sub>(μ-L)] where L is Ph<sub>2</sub>PC<sub>2</sub>H<sub>4</sub>N, which contains the diaxially co-ordinated 2-pyridyldiphenylphosphine bridge were performed. The pyridine rapidly transferred between two Os atoms while the P atom remained firmly co-ordinated to the third Os. Signals for the 6-H protons of the pyridyl ring indicated free and co-ordinated groups.

## Reactions of Dicarboxylic Acids with [Ru(CO)<sub>2</sub>(PPh)<sub>2</sub>]

M. PIZZOTTI, S. CENINI and F. PORTA, *J. Organomet. Chem.*, 1993, 448, (1–2), 205–209

H<sub>2</sub>O soluble Ru and Pt complexes were obtained by reaction of [Ru(CO)<sub>2</sub>(PPh)<sub>2</sub>] and dicarboxylic acid. The derivative obtained with oxalic acid [Ru(O<sub>2</sub>CCO<sub>2</sub>H)<sub>2</sub>(CO)<sub>2</sub>(PPh)<sub>2</sub>] dissolved in H<sub>2</sub>O when treated with NEt<sub>3</sub>, and reacted with [Pt(PPh)<sub>3</sub>] to yield [Ru(CO)<sub>2</sub>(PPh)<sub>2</sub>](μ-O<sub>2</sub>CCO<sub>2</sub>)<sub>2</sub>Pt(PPh)<sub>3</sub>, which was unstable in solution.

## ELECTROCHEMISTRY

### Reduction of Acids at a Platinum Ultramicroelectrode: Application to “in situ” Acid Number Control of Fluid Lubricants (Phosphate Esters)

M. PERDICAKIS, C. PIATNICKI, M. SADIK, R. PASTURAUD, B. BENZAKOUR and J. BESSIÈRE, *Anal. Chim. Acta*, 1993, 273, (1–2), 81–91

Studies of the effect of the addition of a supporting electrolyte on the limiting currents of acids at a Pt ultramicroelectrode gave details about their charge, dissociation and polyacidic character. Acid-base reactions in tributyl phosphate can be followed without adding a supporting electrolyte, even if the dielectric constant was low. The acidity of phosphate esters used as lubricants can be monitored by amperometry at the Pt ultramicroelectrode without disturbance to the medium.

## Electrochemical Behavior of Pt-Modified Cobalt Oxide Electrodes in NaOH Solutions under Oxygen Atmosphere

S. WADA, K. NISHIMURA, K. YAHIKOZAWA, M. ENYO and Y. TAKASU, *Chem. Lett. Jpn.*, 1993, (1), 45–48

Synergistic effect for Pt-modified Co oxides (Pt + Co<sub>3</sub>O<sub>4</sub>) electrodes, prepared from H<sub>2</sub>PtCl<sub>6</sub> and Co(NO<sub>3</sub>)<sub>2</sub> by pyrolysis, was studied in NaOH solutions under O<sub>2</sub> atmosphere. The results showed that Pt atoms or small cluster particles deposited on Co<sub>3</sub>O<sub>4</sub> oxide particles are in a highly oxidised state, Pt(IV). Glassy C-supported Pt + Co<sub>3</sub>O<sub>4</sub> electrodes of ~10 mol% Pt exhibited the equilibrium O electrode potential and electrocatalytic activity toward the O<sub>2</sub> reduction in O<sub>2</sub>-saturated 1 mol/dm<sup>3</sup> NaOH solutions.

## Temperature Dependence of the Tafel Slope for Oxygen Reduction on Platinum in Concentrated Phosphoric Acid

S. J. CLOUSER, J. C. HUANG and E. YEAGER, *J. Appl. Electrochem.*, 1993, 23, (6), 597–605

A bright Pt rotating disc was used to examine O reduction in concentrated H<sub>3</sub>PO<sub>4</sub> at 25–250°C and O pressures up to 1.77 MPa; and cyclic voltammetry was used to study the anodic film formed on Pt in concentrated H<sub>3</sub>PO<sub>4</sub>, and possible electroreduction of H<sub>3</sub>PO<sub>4</sub> on Pt. It was found that the apparent transfer coefficient for the O reduction was approximately proportional to temperature, instead of independent of temperature, and possible reasons are suggested.

## The Electrocatalytic Behaviour of Palladium in Acid and Base

L. D. BURKE and J. K. CASEY, *J. Appl. Electrochem.*, 1993, 23, (6), 573–582

Working and counter electrodes of Pd were made and examined in 1.0 M H<sub>2</sub>SO<sub>4</sub> and NaOH at 25°C. The smooth working electrodes were coated with Pd black, and the reactions were performed by cyclic voltammetry. An unusual peak at ~0.23 V vs. RHE was observed for Pd in acid, similar to one which occurs in Pt. The electrocatalytic activity of Pd is somewhat similar to that of Pt, but its activity is lower in many cases and its stability in acid is significantly lower.

## A Mixture Design Approach to the Service Life and the Oxygen Evolving Catalytic Activity of Ru-Sn-Ti Ternary Oxide Coated Electrodes

S.-M. LIN and T.-C. WEN, *J. Appl. Electrochem.*, 1993, 23, (5), 487–494

Ternary oxide coatings of Ru-Sn-Ti on Ti substrates were examined for effects of calcination temperature and coating solution on service life and electrode oxygen evolving catalytic activity (OECA), and subjected to regression analysis. For electrodes calcined at 400°C, 55–60% Ru content gave maximum service life, while for those calcined at 500°C only 30–55% Ru content was necessary for long service lives. The OECA of an RuO<sub>2</sub> coated electrode decreased with increasing Ti and Sn content and the activity and service lives of Ru-Sn binary electrodes were higher than for Ru-Ti.

### Oxidation Kinetics of a Ru(bpy)<sub>3</sub><sup>3+</sup> Derivative in Langmuir-Blodgett Layers. Comparison to Ru(bpy)<sub>3</sub><sup>3+</sup> in Homogeneous Solutions

J. RABANI, K. HASHIMOTO, Z. F. LIU and A. FUJISHIMA, *Langmuir*, 1993, 9, (3), 818-823

Studies were performed of the chemical kinetics of redox reactions in a Langmuir-Blodgett monolayer containing a Ru(bpy)<sub>3</sub><sup>3+</sup> derivative. The oxidation rates of RuC<sub>60</sub><sup>3+</sup> films with a series of reducing reactants were studied spectrophotometrically and compared to the reactivity of Ru(bpy)<sub>3</sub><sup>3+</sup> with the same solutes in homogeneous solutions. The regeneration of the Ru(II) spectrum obeyed a first-order law, the rate of which increased linearly with solute concentration.

### In-situ Spectroscopic Voltammetry Investigations of the Formation of a Water Oxidation Catalyst [(bpy)<sub>2</sub>(H<sub>2</sub>O)Ru-O-Ru(H<sub>2</sub>O)(bpy)]<sup>4+</sup> at a Nafion-Coated Electrode

R. RAMARAJ, A. KIRA and M. KANEKO, *J. Electroanal. Chem.*, 1993, 348, (1 and 2), 367-376

The monomeric complex *cis*-[Ru(bpy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> was adsorbed on a Nafion film coated onto an indium tin oxide electrode. Spectroscopic voltammetric studies at different pH conditions showed that the monomeric complex in the Nafion film dimerises upon oxidation to yield the corresponding oxo-bridged title complex, which is a water oxidation catalyst. The reversible formation of the dimer and monomer during oxidation and reduction of the corresponding complexes at appropriate potentials was established.

## PHOTOCONVERSION

### Photocatalytic Micropatterning of Titanium Oxide Surface with Platinum

H. SUGIMURA, T. UCHIDA, N. KITAMURA and H. MASUHARA, *Chem. Lett. Jpn.*, 1993, (2), 379-382

Platinum micropatterns were fabricated photocatalytically on TiO<sub>2</sub> surface by projecting a reduced light image of a photomask. Negative and positive Pt patterns on TiO<sub>2</sub> with the spatial resolution > 10 μm were obtained by photoreduction of PtCl<sub>4</sub><sup>2-</sup> to Pt in aqueous K<sub>2</sub>PtCl<sub>6</sub> solution and photoetching of the deposited Pt in aqueous HCl solution, respectively.

### Degradation of Formic Acid over Semiconducting Membranes Supported on Glass: Effects of Structure and Electronic Doping

M. A. AGUADO and M. A. ANDERSON, *Solar Energy Mater. Solar Cells*, 1993, 28, (4), 345-361

The photocatalytic oxidation of HCOOH solutions over supported semiconducting TiO<sub>2</sub> ceramic membranes doped with Pt, RuO<sub>2</sub>, Li, Mg, V and Mo has been investigated. Sol-gel techniques were used to coat pyrex glass with colloidal solutions, followed by firing to form photocatalysts. The most active TiO<sub>2</sub> photocatalysts are those with the least number of boundaries between particles

### Photophysics and Photosensitization Behavior of Microcrystalline [Pt(bpy)<sub>2</sub>][Pt(pop)<sub>4</sub>].nH<sub>2</sub>O

R. PALMANS, A. J. FRANK, V. H. HOULDING and V. M. MISKOWSKI, *J. Mol. Catal.*, 1993, 80, (3), 327-340

The photophysics and photosensitising properties of the insoluble double salts of the title complex ("PBPop"; pop = H<sub>2</sub>P<sub>2</sub>O<sub>5</sub><sup>2-</sup>), were examined after preparation of the complex. The initial orange complex dehydrated readily and irreversibly to a yellow form, which displayed very intense emission, with a room temperature lifetime of 45 ns and an estimated radiative rate constant of 70,000/s. Powder suspensions of both forms of PBPop were active as photosensitisers for generating H<sub>2</sub> from aqueous solution of a colloidal Pt catalyst and ethylenediaminetetraacetate as an electron donor.

### New Sensitizing Relay Compounds for H<sub>2</sub> Production

R. BAUER and C. KÖNIGSTEIN, *Int. J. Hydrogen Energy*, 1993, 18, (3), 205-210

New electron relay materials: 1,1",1'''-trialkyl-[4,2';4',4'';6',4'''] quaterpyridinium trichloride, etc., with sensitiser and electron relay properties were tested in conjunction with Pt catalyst of particle size ~3 nm, EDTA and acetate buffer for H<sub>2</sub> production from water on exciting the systems with near-UV light. Quantum yields of ~2% were obtained. Only electron relay compounds with a pyridinium ring with a free electron pair could produce H<sub>2</sub> without dye stuff.

### Effect of Carbon Monoxide Pressure on the Nature of Active Centres on Photocatalytic Conversion of Pentane in the Presence of Rhodium(I) Bis(trimethylphosphine)carbonylchloride

N. K. KHANNANOV, G. N. MENCHIKOVA and E. A. GRIGORYAN, *Kinet. Katal.*, 1993, 34, (1), 63-67

Comparative studies of photocatalytic dehydrogenation and carbonylation of pentane in the presence of RhCl(PMe<sub>3</sub>)<sub>2</sub>(CO) (I) were performed by kinetic and spectral techniques. It is shown that at CO pressure of 0-60 mm Hg, the dehydrogenation is nearly totally suppressed, while the carbonylation rate is at a maximum. The kinetic dependence at the CO pressure was described as a photocatalytic process scheme formed from (I) after photoseparation of CO from alkylhydride and acylhydride intermediates.

### Photophysics of Ru(II)- and Os(II)-Polypyridine Complexes in Poly(ethylene-oxide) Matrices

S. CAMPAGNA, A. BAROLOTTA and G. DI MARCO, *Chem. Phys. Lett.*, 1993, 206, (1,2,3,4), 30-36

The photophysical properties of Ru(bpy)<sub>3</sub><sup>3+</sup>, Ru(bpy)<sub>2</sub>(biq)<sup>2+</sup> and Os(bpy)<sub>3</sub><sup>3+</sup> where bpy is 2,2'-bipyridine and biq is 2,2'-biquinoline, in the title PEO matrices constituted by a repeating unit of average molecular weight 400, (PEO-400 a highly viscous fluid) and 600000 dalton, (PEO-600000, a semicrystalline solid) were studied at ambient and 77K.

### Excited State Energy of (<sup>3</sup>MLCT)Ru(bpy)<sub>3</sub><sup>2+</sup> by Time-Resolved Thermal Lens and Photoacoustic Methods in Aqueous Solutions

X. SONG and J. F. ENDICOTT, *Chem. Phys. Lett.*, 1993, 204, (5,6), 400–406

The time-resolved thermal lens technique and the pulsed photoacoustic microcalorimetric technique, were used to determine the thermally averaged charge transfer excited state energy of Ru(bpy)<sub>3</sub><sup>2+</sup> in ambient aqueous solutions. The averaged excited state energy of (<sup>3</sup>MLCT)Ru(bpy)<sub>3</sub><sup>2+</sup> was (16.8 ± 0.2) × 10<sup>3</sup>/cm and (17.0 ± 0.6) × 10<sup>3</sup>/cm, by the photoacoustic and the thermal lens methods, respectively.

### Photoresponsive Bilayer Membranes Composed of Ru(bpy)<sub>3</sub><sup>2+</sup> and Methylviologen-Containing Layers Sandwiched between ITO Electrodes

G.-J. YAO, T. ONIKUBO and M. KANEKO, *Electrochim. Acta*, 1993, 38, (8), 1093–1096

A new sandwich type photoresponsive bilayer polymer device, which utilised the photochemical reaction between Ru(bpy)<sub>3</sub><sup>2+</sup> and methylviologen (MV<sup>2+</sup>) confined in each Nafion layer, was fabricated. This photochemical diode, ITO/Nafion[Ru(bpy)<sub>3</sub><sup>2+</sup>]/Nafion[MV<sup>2+</sup>]/ITO, generated a cathodic photocurrent with respect to the Ru complex-coated electrode. Higher membrane thickness induced higher photocurrent density within each layer.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Pulsed Laser Deposition of Heteroepitaxial Thin Pt Films on MgO(100)

J. F. M. CILLESSEN, R. M. WOLF and D. M. DE LEEUW, *Thin Solid Films*, 1993, 226, (1), 53–58

Studies of pulsed laser ablation deposition of Pt thin films deposited on MgO(100) showed that the deposited films grew epitaxially with a Pt(111) XRD intensity of < 0.5% than that of the Pt(200) reflection in the films. The layers obtained were very smooth and without voids above a critical layer thickness which depended strongly on the deposition temperature. There was a complete alignment between the in-plane lattice vectors of Pt and MgO.

### Effect of Sputter-Deposition Processes on the Microstructure and Magnetic Properties of Pt/Co Multilayers

P. F. GARCIA, Z. G. LI and W. B. ZEPER, *J. Magn. & Magn. Mater.*, 1993, 121, (1–3), 452–460

The relationship of magnetic properties and synthesis of sputtered Pt/Co multilayers to their microstructure was studied by high resolution electron microscopy. Growing the Pt/Co multilayers by low energy sputtering enhanced their (111)-f.c.c. texture and produced a large perpendicular magnetic anisotropy. Sputter etching substrates before multilayer deposition also promoted (111) texture and anisotropy.

### Studies of Platinum Electroplating Baths. Part II. Deposition of Platinum from a Solution of Pt(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup> in Aqueous Acid

A. J. GREGORY, W. LEVASON and D. PLETCHER, *J. Electroanal. Chem.*, 1993, 348, (1 and 2), 211–219

Studies of stability of Pt(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup> showed that this Pt(II) species was completely stable in 1 mol/dm<sup>3</sup> aqueous acids and its reduction was simple, although irreversible. Adherent and reflective deposits of Pt metal were formed on a Cu panel from solutions of Pt(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup> in 1 mol/dm<sup>3</sup> HClO<sub>4</sub>, even at room temperature. It is suggested that the limiting current density could be increased by a factor of > 100 with a Pt electroplating bath being based on Pt(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup> having the current density of > 100 mA/cm<sup>2</sup>.

### Simultaneous Deposition of Pd and Ag on Porous Stainless Steel by Electroless Plating

J. SHU, B. P. A. GRANDJEAN, E. GHALI and S. KALLIAGUINE, *J. Membrane Sci.*, 1993, 77, (2+3), 181–195

Studies of the co-deposited behaviour of Pd and Ag on porous stainless steel by electroless plating showed passivation of simultaneous deposition of Pd and Ag by the preferential deposition of Ag in an electroless bath containing EDTA as a complexing agent. However, Pd and Ag can be successfully co-deposited after effective activation of the substrate by Pd pre-deposition. Co-deposited Pd and Ag are in separate phases with small amounts of an amorphous Pd-rich phase present in the deposited material.

### Photopatterning and Selective Electroless Metallization of Surface-Attached Ligands

W. J. DRESSICK, C. S. DULCEY, J. H. GEORGER and J. M. CALVERT, *Chem. Mater.*, 1993, 5, (2), 148–150

Organosilanes possessing ligating functions were chemisorbed on various surfaces as films of monolayer thickness, and the resulting surface selectively binds Pd(II) from solution. The bound Pd(II) functions as an electroless catalyst for the deposition of patterned metal films, which are useful in microlithographic application. Patterned deep UV irradiation selectively destroys the ligating ability in the irradiated regions of the film.

## APPARATUS AND TECHNIQUE

### A Quantitative Detector for Thin-Layer Chromatography Based on Voltammetry at a Pt Microwire Electrode

I. SMALERA and I. F. CHENG, *Microchem. J.*, 1993, 47, (1/2), 182–186

A quantitative electrochemical detector device for thin-layer chromatography (TLC) is based on the voltammetric detection of the solute species at a Pt microwire electrode during TLC plate development. The resulting current response gives a detection limit of 40 ng for a ferrocene solute species. The ferrocene samples were spotted onto SiO<sub>2</sub> gel plates and the Pt wire surface was treated after each run by placing in a hot HNO<sub>3</sub> bath for 30 seconds.

### **Planar Type of Carrier Catalytic Methane Sensor**

P. YE and H. DONG, *Sens. Actuators B*, 1993, **12**, (1), 19–22

A planar type of carrier has been developed for a catalytic methane sensor. A layer of thin Pt film was sputtered onto a suitable substrate, and by etching a spiral Pt film resistance of 50–100  $\Omega$  was made. A pair of lead windows is made to the terminals of the Pt film resistance, which are spot-welded for connection to the external legs to provide a complete chip. The chip is then covered by crystalline alumina. The new device has excellent linearity, sufficient sensitivity, a low operating current and temperature.

### **Shipboard Investigation of DOC in the NE Atlantic Using Platinum-Based Catalysts in a Shimadzu TOC-500 HTCO Analyser**

A. E. J. MILLER, R. F. C. MANTOURA and M. R. PRESTON, *Mar. Chem.*, 1993, **41**, (1–3), 215–221

Various Pt catalysts were evaluated on board ship for their high temperature catalytic oxidation efficiencies for the conversion of dissolved organic C (DOC) to CO<sub>2</sub> in samples taken from the upper 300 m of the NE Atlantic Ocean. Catalysts were sometimes used with scrubbers to remove interfering gaseous by-products (Cl<sub>2</sub>, S and CO). The 100 % Pt catalyst generally oxidised the greatest proportion of oceanic DOC, although all the catalysts produced DOC concentrations of 90–210  $\mu\text{M C}$ .

### **Screen Printed Glucose Electrodes Based on Platinised Carbon Particles and Glucose Oxidase**

M. F. CARDOSI and S. W. BIRCH, *Anal. Chim. Acta*, 1993, **276**, (1), 69–74

Silk screen printing was used to see if disposable strip enzyme electrodes could be produced from platinised Vulcan XC-72 C particles. The electrodes had the electrocatalytic activity of metal microparticles with the optimum features of mass produced screen printed sensors. Glucose oxidase was immobilised on the surface of the particles, allowing the biocatalytic reaction to be linked to oxidation of the liberated H<sub>2</sub>O<sub>2</sub>, giving a glucose detection limit of  $2 \times 10^{-5} \text{ M}$ .

### **Effect of Relative Humidity on the Performance of a Platinum-Lead Denuder for the Adsorption of Nitrobenzene**

C. L. P. THOMAS and J. F. ALDER, *Anal. Chim. Acta*, 1993, **274**, (1), 171–177

A Pt-Pb coated annular denuder was tested with humid atmospheres of 20–99% relative humidity at 12.5°C laden with 16  $\mu\text{g}/\text{m}^3$  nitrobenzene. A dramatic effect from the high relative humidity on the performance of the denuder was seen, especially at > 47% relative humidity. The capacity of the denuder tube decreased linearly by 1.2% for each 1% increase in relative humidity at 12.5°C. It is suggested that the presence of multilayers of sorbed H<sub>2</sub>O on the metal surface causes the reduced efficiency of the denuder.

### **Luminescent Porphyrins as Probes for Optical (Bio)sensors**

D. B. PAPKOVSKY, *Sens. Actuators B*, 1993, **11**, (1–3), 293–300

Recent applications of porphyrin probes in optical (bio)sensors, with special emphasis on phosphorescent Pt- and Pd porphyrins, mainly in quenched luminescence O<sub>2</sub> sensors, are discussed and compared to the other fluorescent probes and optical sensing systems. Sensing based on O probes using quenched-luminescence are described: (1) a flow-injection glucose sensor, (2) luminescent solid-state O<sub>2</sub>-sensitive compositions and membranes, (3) glucose membranes on the basis of O membrane, (4) a flow cell with an enzyme column and O optrode for determination of polyphenols.

### **Investigations of a Gas Sensor with Integrated Metal-Oxide Semiconductor Structure**

X. DING, H. YU and H. JIN, *Sens. Actuators B*, 1993, **12**, (1), 1–4

The sensitive mechanism of a Pd-gate MOS gas sensor is described. CO-sensitive and H<sub>2</sub>-sensitive elements, a selective differential element, a heating element and temperature-sensitive element were integrated in one chip by using an n-well compatible process for MOS and bipolar transistors. A chip-temperature constant system, which has high stability at a tuneable high temperature, has been developed.

### **Atomization of Tin in Saline Water Media in Graphite Furnace Atomic Absorption Spectrometry with a Tungsten-Coated Tube Using Palladium as a Chemical Modifier**

E. IWAMOTO, H. SHIMAZU, K. YOKOTA and T. KUMAMARU, *Anal. Chim. Acta*, 1993, **274**, (2), 231–235

The determination of Sn in sea water can be measured by graphite furnace atomic absorption spectrometry. The combined use of a W-coated non-pyrolytic graphite tube and Pd as a chemical modifier eliminated salinity in doubly diluted sea H<sub>2</sub>O, during direct atomisation of Sn in saline H<sub>2</sub>O, without a serious loss of Sn at an ashing temperature of 1700°C. Sulphate interference was also suppressed.

### **Analytical Utility of the Iridium-Based Mercury Ultramicroelectrode with Square-Wave Anodic Stripping Voltammetry**

S. P. KOUNAVES and W. DENG, *Anal. Chem.*, 1993, **65**, (4), 375–379

The characteristics of an Ir based Hg ultramicroelectrode with square-wave anodic stripping voltammetry, for the analysis of Cu, Cd and Pb in water samples was studied. Peak stripping currents varied linearly with deposition times from 1–1200 s. Peak potentials and current were unchanged with electrolyte concentration of 1–10<sup>-3</sup> M. The electrode gave a rapid, accurate, sensitive method for the determination of metals ions in aqueous solutions without deoxygenation, added electrolyte or stirring.

## Gas Sensing Using Langmuir-Blodgett Films of a Ruthenium Porphyrin

D.-G. ZHU, D.-F. CUI, M. C. PETTY and M. HARRIS, *Sens. Actuators B*, 1993, 12, (2), 111–114

Langmuir-Blodgett films of a Ru porphyrin complex: 2,3,7,8,12,13,18-octaethyl-21H, 23H-porphine Ru(II) carbonyl, one-to-one complex with tetrahydrofuran, Ru(OEP), have been formed and properties determined. Up to 70 layers of the material could be transferred from the water surface to a variety of substrates reproducibly. The thickness per layer was  $1.65 \pm 0.05$  nm. The LB layers exhibited semiconducting electrical behaviour with a thermal activation energy for conduction of  $0.72 \pm 0.02$  eV between 20 and 100°C. On exposure to NO<sub>2</sub> the conductivity increased.

## HETEROGENEOUS CATALYSIS

### Influence of Metal Particle Size and Effect of Gold Addition on the Activity and Selectivity of Pt/Al<sub>2</sub>O<sub>3</sub> Catalysts in the Reduction of Nitric Oxide by Methane

M. C. DEMICHELI, L. C. HOANG, J. C. MÈNÈZO, J. BARBIER and M. PINABIAU-CARLIER, *Appl. Catal. A: Gen.*, 1993, 97, (1), L11–L17

The structure sensitivity of Pt/Al<sub>2</sub>O<sub>3</sub> catalysts with various metallic dispersions for NO reduction by methane in He, at 250–350°C, was studied. With monometallic Pt the specific reaction rate increased with increasing particle size from 1.5 to 15 nm, showing that the reaction preferentially occurs on large Pt planes. Au was deposited on the Pt on low co-ordination sites for use as a model catalyst.

### Performance of Platinum-Group Metal Catalysts for the Selective Reduction of Nitrogen Oxides by Hydrocarbons

A. OBUCHI, A. OHI, M. NAKAMURA, A. OGATA, K. MIZUNO and H. OHUCHI, *Appl. Catal. B: Environ.*, 1993, 2, (1), 71–80

The performance of Pt, Pd, Ir, Rh and Ru supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was studied for the selective reduction of NO<sub>x</sub> by hydrocarbons. Pt and Rh had high NO<sub>x</sub> conversion activities in model mixtures and in diesel exhaust gases, especially at 200–350°C. Pt-Rh and Pt catalysts have higher activity and durability than a Cu/ZMS-5 catalyst for real diesel exhaust conditions. However, the Pt containing catalysts produced more N<sub>2</sub>O than N<sub>2</sub>.

### A Novel Method in Preparation of Pt/KL Catalyst for Aromatization of Hexane

L.-X. DAI, H. SAKASHITA and T. TATSUMI, *Chem. Lett. Jpn.*, 1993, (2), 387–390

The addition of KCl to Pt/KL catalyst prepared by ion exchange resulted in higher activity and selectivity for benzene formation than catalyst prepared by co-impregnation of KL zeolite with [Pt(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub> and KCl. When the Cl:Pt molar ratio was 3.3, hexane was obtained in 99.8% conversion and a benzene yield of 88.3%, under a pressure of 0.3 MPa.

### Improvement of Platinum-Supported Zeolite Catalysts for *n*-Hexane Aromatization by Halocarbon Treatment and Alkaline Soaking

M. SUGIMOTO, H. KATSUNO and T. MURAKAWA, *Appl. Catal. A: Gen.*, 1993, 96, (2), 201–216

Studies of the effects of alkaline compound and halocarbon treatments on the catalytic activities of Pt supported on zeolite Y, mordenite and zeolite L showed that the activity and selectivity for *n*-hexane aromatization increased with the decreasing acidities of the zeolite supports. An alkaline soaking treatment for mordenite increased the activities for *n*-hexane aromatization. Soaking treatments may decrease the electron deficiency of Pt particles supported on mordenite.

### Activity and Selectivity of PtNi/TiO<sub>2</sub> Catalysts for Hydrogenation of Crotonaldehyde

C. G. RAAB and J. A. LERCHER, *Catal. Lett.*, 1993, 18, (1,2), 99–109

Studies of the hydrogenation of crotonaldehyde on PtNi/TiO<sub>2</sub> catalysts showed that Pt/TiO<sub>2</sub> was most active during hydrogenation of the C=O bond of crotonaldehyde. With the addition of Ni to Pt, the activity for carbonyl group hydrogenation decreased while hydrogenation of the C=C bond increased. Two different types of sites were found to be active for C=O bond hydrogenation, the Pt-TiO<sub>2</sub> interface and the PtNi bimetallic phase.

### Interaction of CO with Platinum Species in Zeolites. Evidence for Platinum Carbonyls in Partially Reduced Zeolite PtNaX

H. BISCHOFF, N. I. JAEGER, G. SCHULZ-EKLOFF and L. KUBELKOVA, *J. Mol. Catal.*, 1993, 80, (1), 95–103

IR spectral studies of the decomposition of Pt(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> in zeolite NaX both in vacuum and in flowing O showed a variety of ionic species PtO<sub>2</sub>, Pt<sup>4+</sup>, Pt<sup>2+</sup>-CO and [Pt(CO)]<sup>+</sup> complexes formed after the adsorption of CO at 300 K. Subsequent reduction with H resulted in characteristic particle size distributions, which are reflected in distinct vibration frequencies of adsorbed CO, ~2010/cm for  $d \approx 1.2$  nm (supercage size) and ~2070/cm for  $d \approx 4$  nm. A hydrated precalined sample treated with CO showed unusual low Pt carbonyl bands assigned to [Pt<sub>3</sub>(CO)<sub>6</sub>]<sup>2+</sup> clusters, supported on Pt<sup>2+</sup>/PtO.

### Ligand-Stabilized Giant Palladium Clusters: Promising Candidates in Heterogeneous Catalysis

G. SCHMID, M. HARMS, J.-O. MALM, J.-O. BOVIN, J. VAN RUITENBECK, H. W. ZANDBERGEN and W. T. FU, *J. Am. Chem. Soc.*, 1993, 115, (5), 2046–2048

Large ligand-stabilised clusters were formed when Pd(II) acetate was reduced by H<sub>2</sub> in acetic acid solution containing ligands. Clusters were produced of idealised formula Pd<sub>56</sub>phen<sub>36</sub>O<sub>200±10</sub> (phen = phenanthroline) at < 10 %. For the other 90 % of Pd, a mixture of mainly two different cluster with diameters of 31.5 and 36.0 Å were located of calculated formulae: Pd<sub>1415</sub>phen<sub>60</sub>O<sub>-1100</sub> and Pd<sub>2057</sub>phen<sub>84</sub>O<sub>-1600</sub>.

### Catalytic Reduction of Nitric Oxide on PdO-MoO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>

I. HALASZ, A. BRENNER and M. SHELEF, *Appl. Catal. B: Environ.*, 1993, 2, (1), 131-146

The title catalyst containing 2 % Pd and 20 % Mo was studied for NO reduction by CO, H<sub>2</sub> and by a CO + H<sub>2</sub> mixture, in various amounts of O<sub>2</sub> at 25-550°C. The Pd determined the performance of catalysts under O<sub>2</sub> free reaction conditions up to 400°C. At higher temperatures the MoO<sub>3</sub> improves the catalyst performance. For CO + H<sub>2</sub> reduction the selectivity and activity are unlike those of monometallic catalysts in the presence of O<sub>2</sub>. NO is reduced selectively to N<sub>2</sub> and N<sub>2</sub>O at > 70 % conversion at 300-550°C.

### Palladium Polymer Catalysts in Reduction Reactions of Acetaminic Cinnamic Acid Azlactone and Its Solvolysis Products

E. I. KARPEISKAYA, L. F. GODUNOVA, E. S. LEVITINA, M. R. LYUBEZNOVA, E. I. KLABUNOVSKII, E. S. SHPIRO, G. N. BAEVA, E. D. LUBUZH, L. B. KRENTCEL, A. D. LITMANOVICH and N. A. PLATE, *Izv. Akad. Nauk (Russ.)*, *Ser. Khim.*, 1992, (10), 2368-2380

Pd complexes of linear and cross-linked copolymers of R, S-, R- and S-1-(4-vinylphenyl)ethylamine with styrene and divinylbenzene were obtained. The chiral polymeric catalysts were more active in reductive hydrolysis than those obtained in the absence of a polymer. The catalysts did not show enantioselective properties.

### Kinetics and Product Composition for Methane Oxidation by PdSO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub>/SiO<sub>2</sub> System at 220°C

V. P. TRET'YAKOV, L. K. VOLKOVA and E. S. RUDAKOV, *Kinet. Katal.*, 1993, 34, (1), 90-92

Studies showed that Pd sulphate deposited on silicate together with H<sub>2</sub>SO<sub>4</sub>, in the PdSO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub>/SiO<sub>2</sub> system, at 220°C oxidises methane forming CO<sub>2</sub> while H<sub>2</sub>SO<sub>4</sub> is reduced to SO<sub>2</sub>, yielding 25 and 50 mol% of CO<sub>2</sub> and SO<sub>2</sub>, respectively. During treatment with HCl, a study of the gaseous phase in the reactor after total CH<sub>4</sub> conversion showed methyl chloride.

### Synthesis Gas Formation by Direct Oxidation of Methane over Rh Monoliths

D. A. HICKMAN, E. A. HAUPFEAR and L. D. SCHMIDT, *Catal. Lett.*, 1993, 17, (3,4), 223-237

The production of H<sub>2</sub> and CO by partial catalytic oxidation of CH<sub>4</sub> in air or O<sub>2</sub> at atmospheric pressure has been examined over Rh coated monoliths at 10<sup>-4</sup>-10<sup>-2</sup> s residence times and compared to known results for Pt coated monoliths. Using O<sub>2</sub> selectivities (S<sub>H</sub>) for H<sub>2</sub> as high as 90 % and CO selectivities of 96 % can be obtained for Rh. With air at room temperature S<sub>H</sub> values are 70 % for Rh and 40 % for Pt. Optimal selectivities for Pt or Rh can be improved by increasing the adiabatic reaction temperature by preheating the reactant gases or using O<sub>2</sub> instead of air.

### Microstructural and Chemical Properties of Ceria-Supported Rhodium Catalysts Reduced at 773 K

S. BERNAL, F. J. BOTANA, J. J. CALVINO, M. A. CAUQUI, G. A. CIFREDO, A. JOBACHO, J. M. PINTADO and J. M. RODRÍGUEZ-IZQUIERDO, *J. Phys. Chem.*, 1993, 97, (16), 4118-4123

Studies of the chemical and microstructural characterisation of a series of Rh/CeO<sub>2</sub> catalysts were made on catalysts prepared using three CeO<sub>2</sub> with different BET surface areas, as well as two metal precursor salts, Rh(NO<sub>3</sub>)<sub>3</sub> and RhCl<sub>3</sub>. Great changes in the chemistry of the H<sub>2</sub>-(Rh/CeO<sub>2</sub>) system were observed when the reduction temperature increased from 623 to 773 K. High-resolution TEM reveals an epitaxial growth of the Rh microcrystal on CeO<sub>2</sub>.

### Iron-Ruthenium Catalyst for the Water-Gas Shift Reaction

A. BASIŃSKA and F. DOMKA, *Catal. Lett.*, 1993, 17, (3,4), 327-332

Fe-Ru catalysts prepared by impregnation of the calcination products of α-, β-, γ- and δ-FeOOH with RuCl<sub>3</sub> or Ru red were tested for the water-gas shift reaction at 350°C. Very active catalysts comprised those based on the calcination products of α- and δ-FeOOH.

### Reactions of Hydrocarbons over Ru/SiO<sub>2</sub>: Exchange with Deuterium and the Onset of Hydrogenolysis

R. BROWN and C. KEMBALL, *J. Chem. Soc., Faraday Trans.*, 1993, 89, (3), 585-594

Studies of exchange reactions with D of a number of selected hydrocarbons such as CH<sub>4</sub>, propane, 2-methylpropane, etc., over a Ru/SiO<sub>2</sub> catalyst, were performed by mass spectroscopy. A strong hydrocarbon-Ru interaction occurred which resulted in temperature increases, relatively easy exchange but with self-poisoning, followed by hydrogenolysis, which was again subject to self-poisoning.

## HOMOGENEOUS CATALYSIS

### Influence of the Reaction Temperature on the Enantioselection of Styrene Hydroformylation Catalyzed by PtCl<sub>2</sub>(SnCl<sub>4</sub>) Complexes of p-Aryl-Substituted Chiral Ligands

I. TÓTH, I. GUO and B. E. HANSON, *Organometallics*, 1993, 12, (3), 848-852

The asymmetric hydroformylation of styrene catalysed by PtCl<sub>2</sub>(SnCl<sub>4</sub>) complexes of (-)-(2S,4S)-2,4-bis[bis(p-(dimethylamino)phenyl)phosphino]pentane (1), (-)-(2S,3S)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis[bis(p-(dimethylamino)phenyl)phosphino]butane (2), etc., were strongly dependent on temperature. With 1 and 2 as the catalysts, a reversed product configuration occurred at 53 and 72°C, respectively. Complex 1 gave 56.7% ee in the R product at 100°C and 60.6% ee in the S product at 30°C.



## Palladium-Catalyzed Hydrocarboxylation of Alkynes with Formic Acid

D. ZARGARIAN and H. ALPER, *Organometallics*, 1993, 12, (3), 712–724

Alkynes were hydrocarboxylated with formic acid in the presence of catalytic amounts of Pd(OAc)<sub>2</sub> and phosphine ligands under 120 psi of CO pressure and 100–110°C to produce the corresponding unsaturated carboxylic acids in 60–90% yields. The regioselectivity is ~90:10 in favour of CR(COOH)=CH<sub>2</sub> when R is a phenyl or a straight chain alkyl, and (*E*)-CHR=CH(COOH) is the major product when R is *t*-Bu and the exclusive one when R is SiMe<sub>3</sub>. The most suitable ligands were PPh<sub>3</sub> and dppb (1,4-bis(diphenylphosphino)butane). A reaction mechanism was proposed which involved the addition of the O-H bond of formic acid to the Pd centre, forming a cationic hydrido(alkyne)Pd intermediate.

## Highly Active Pd(0) Catalyst from Pd(OAc)<sub>2</sub>-Bu<sub>3</sub>P Combination in Untapped 1:1 Ratio: Preparation, Reactivity, and <sup>31</sup>P-NMR

T. MANDAI, T. MATSUMOTO, J. TSUJI and S. SAITO, *Tetrahedron Lett.*, 1993, 34, (15), 2513–2516

The reaction of Pd(OAc)<sub>2</sub> with Bu<sub>3</sub>P in a 1:1 ratio in benzene or THF gave a very active zerovalent Pd species which appeared as a pale yellow solution. The activity of this is discussed on the basis of the significant difference in catalytic reactivity and <sup>31</sup>P{<sup>1</sup>H}-NMR features between such a catalyst and one prepared from Pd<sub>2</sub>(dba)<sub>3</sub> and excess Bu<sub>3</sub>P.

## Homogeneous Catalytic Acetoxylation of Hexane-1 and Cyclohexane

N. V. TRUSHOVA and A. V. DEVEKLI, *Neftekhimiya*, 1992, 32, (4), 348–353

Studies of acetoxylation of hexane-1 and cyclohexane in the presence of PdCl<sub>4</sub><sup>2-</sup> and nitrate-iodate showed that the catalytic active particles were binuclear  $\pi$ -olefin Pd complexes of the bridge type. It is suggested that the mechanism of formation of monoacetate hexadiol-1,2 and diacetoxycyclohexane differ in the final stage of the trans-formation of acetoxy ion. The acetoxylation process was inhibited by reaction products, insulating the Pd co-ordination sphere.

## Palladium-Catalyzed Sequential Bond Formation Leading to Conjugated Ene-Yne System

S. TORII, H. OKUMOTO, T. TADOKORO, A. NISHIMURA and M. A. RASHID, *Tetrahedron Lett.*, 1993, 34, (13), 2139–2142

The sequential formation of contiguous C-C bonds among sp<sup>2</sup> and sp C was catalysed by Pd(0) catalysts in a single operation to provide a straightforward and convergent synthetic path to the ene-yne system, which is necessary for the structure of the neocarzinostatin (NCS) chromophore. A mixture of a 1,1-dibromoolefin and alkynylstannane, in the presence of Pd(OAc)<sub>2</sub> and toluene, produced cyclisation and coupling to give the ene-yne system in 51% yield.

## Palladium(0)-Catalysed Transfer Hydrogenation of Alkynes to *cis*-Alkenes with HCO<sub>2</sub>H-NEt<sub>3</sub>

K. TANI, N. ONO, S. OKAMOTO and F. SATO, *J. Chem. Soc., Chem. Commun.*, 1993, (4), 386–387

Studies of transfer hydrogenation of alkynes using HCO<sub>2</sub>H-NEt<sub>3</sub> as a H donor in the presence of Pd<sup>0</sup> catalyst using [Pd<sub>2</sub>(dba)<sub>3</sub>]-PBu<sub>3</sub> (dba = dibenzylideneacetone), showed high stereoselectivity to give *cis*-alkenes in excellent yields.

## Reductive Carbonylation of Mono- and Dinitroarenes Catalyzed by Montmorillonitebipyridinylpalladium (II) Acetate and Ruthenium Carbonyl

V. L. K. VALLI and H. ALPER, *J. Am. Chem. Soc.*, 1993, 115, (9), 3778–3779

A highly selective reductive carbonylation of mono- and dinitro aromatic compounds to their corresponding mono- and diurethanes is reported. Montmorillonitebipyridinyl Pd(II) acetate (Pd-clay) coupled with Ru<sub>3</sub>(CO)<sub>12</sub> were used as the dual catalytic system in the presence of bidentate donor ligands, such as 2,2'-bipyridine. No side products were detected. Enhanced surface acidities of the clay upon anchoring may explain the high selectivity.

## New Routes to Isomerically Pure Cyclopentanes. Synthesis of (3*S*,4*S*)-3,4-Bis(benzoyloxymethyl) cyclopentan-1-ol Using Palladium-Catalyzed [2 + 3] Cycloaddition

M. JANSON, I. KVARNSTRÖM, S. C. T. SVENSSON, B. CLASON and B. SAMUELSSON, *Synthesis*, 1993, (1), 129–133

The enantiomerically pure title complex, which is a useful intermediate for the synthesis of a number of natural products, was prepared by two different routes in the presence of Pd(OAc)<sub>2</sub> catalyst. Formation of the chiral five-membered ring was achieved using a Pd-catalysed [2 + 3] cycloaddition between 2-(acetoxymethyl)-3-(trimethylsilyl)propene and optically active methyl (*E*)-3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene- $\alpha$ -D-xylo-hept-5-enofuranuronate or ethyl (4*R*,*Z*)-4,5-(isopropylidenedioxy)pent-2-enoate.

## Interaction of Diazoalkanes and Unsaturated Compounds. II. A Relative Reactivity of Olefins in a Reaction of Catalytic Cyclopropanation by Diazomethane Effected by Palladium Catalysts

U. M. DZHEMILEV, V. A. DOKICHEV, S. Z. SULTANOV, S. L. KHURSAN, O. M. NEFEDOV, YU. V. TOMILOV and A. B. KOSTITSYN, *Izv. Akad. Nauk (Russ.), Ser. Khim.*, 1992, (10), 2353–2361

Studies of the relative reaction ability of unsaturated compounds in catalytic cyclopropanation by diazomethane in the presence of Pd<sup>2+</sup>-based catalysts: Pd(OAc)<sub>2</sub>, Pd(acac)<sub>2</sub> and (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub> were performed by the competitive reaction method. A relationship between the relative reaction ability coefficients of olefins in this reaction, with the co-ordination activity of C=C bonds was found.

### Novel Palladium(II)-Catalyzed Direct Synthesis of Polymers with Oxamide and Urea Linkages

G. M. DAHLEN and A. SEN, *Macromolecules*, 1993, **26**, (7), 1784–1786

A novel Pd(OAc)<sub>2</sub> catalysed carbonylation of  $\alpha$ ,  $\omega$ -diamines leading to the synthesis of polyureas and polymers with both oxamide and urea linkages, the relative proportions of which can be varied is reported. The reactions were carried out under oxidative conditions using iodine as promoter. The ratio of oxamide to urea linkages in the resultant polymers is a function of the added iodine, with the ratio decreasing from 1.5 to 0 with increasing I concentration. The end groups are unreacted amines, so further reactions of the polymers should be possible.

### Palladium Ion Assisted Formation and Metallization of Lipid Tubules

M. MARKOWITZ, S. BARAL, S. BRANDOW and A. SINGH, *Thin Solid Films*, 1993, **224**, (2), 242–247

Transformation of lipid tubules has occurred at pH 5.6, from negatively charged 1,2-bis(tricoso-10,12-diyonyl)-sn-glycero-3-phosphohydroxyethanol, into a rigid, cylindrical structure in the presence of tetraamine Pd (II) chloride. The Pd ions transformed the lipid and functioned as the catalytic centre for the electroless metallisation of Ni and Co. Tubules of 0.07–0.16  $\mu\text{m}$  diameter were formed. Unbound Pd salt was removed by dialysing tubule dispersion against H<sub>2</sub>O. Sustained dialysis prior to metallisation resulted in an increase in the diameter of the tubules. Thin slices of metal coated tubules embedded in epoxy resin were characterised by atomic force and scanning tunneling microscopy.

### Dehydrogenative Silylation of Ketones with a Bifunctional Organosilane by Rhodium-Pybox Catalysts

H. NAGASHIMA, T. UEDA, H. NISHIYAMA and K. ITOH, *Chem. Lett. Jpn.*, 1993, (2), 347–350

Studies of dehydrogenative silylation of ketones with 1,2-bis(dimethylsilyl)ethane catalysed by a mixture of RhCl<sub>3</sub>(pybox) and Ag<sup>+</sup> salts, at 40–50 °C, showed the formation of the corresponding silylenol ether in high yields. Only one Si-H group of 1,2-bis(dimethylsilyl)ethane is converted to the corresponding silyl enol ether.

### A High-Yield Conversion of *trans*-Rh(Cl)(CO)(PPh<sub>3</sub>)<sub>2</sub> to Rh(Cl)(PPh<sub>3</sub>)<sub>3</sub>

J. M. O'CONNOR and J. MA, *Inorg. Chem.*, 1993, **32**, (9), 1866–1867

The high-yield conversion to Rh(Cl)(PPh<sub>3</sub>)<sub>3</sub> (1) of *trans*-Rh(Cl)(CO)(PPh<sub>3</sub>)<sub>2</sub> was achieved by using a diphenylphosphoryl azide (DPPA) as a carbonyl ligand abstraction reagent in a stoichiometric reaction. In solution complex (1) was found to exist in equilibrium with a minor amount of [Rh(PPh<sub>3</sub>)<sub>2</sub>Cl]<sub>2</sub> dimer. There was no evidence of formation of RhCl(PPh<sub>3</sub>)<sub>2</sub>(RNCONR) (R = P(O)(OPh<sub>2</sub>).

### Rhodium-Catalyzed Silylformylation of Aldehydes: A Mild and Efficient Catalytic Route to $\alpha$ -Silyloxyaldehydes

M. E. WRIGHT and B. B. COCHRAN, *J. Am. Chem. Soc.*, 1993, **115**, (5), 2059–2060

[(COD)RhCl]<sub>2</sub> has been found to be a very effective catalyst for the silylformylation of aldehydes. The reaction is very general and works well for heterocyclic and aliphatic systems, affords high yield of the  $\alpha$ -silyloxyaldehydes and does not require the use of excess aldehyde.

### IrCl<sub>2</sub>H(P<sup>t</sup>Pr)<sub>2</sub> as Catalyst Precursor for the Reduction of Unsaturated Substrates

H. WERNER, M. SCHULZ, M. A. ESTERUELAS and L. A. ORO, *J. Organomet. Chem.*, 1993, **445**, (1–2), 261–265

Studies of the catalytic behaviour of the complex IrCl<sub>2</sub>H(P<sup>t</sup>Pr)<sub>2</sub> in the presence of NaBH<sub>4</sub> showed it to be a useful catalyst or catalyst precursor for the reduction of unsaturated organic substrates by H transfer from 2-propanol or direct hydrogenation in H<sub>2</sub>. The Ir complex reacts with H<sub>2</sub> to yield the dihydrido complex IrClH<sub>2</sub>(P<sup>t</sup>Pr)<sub>2</sub>. In the presence of unsaturated substrates such as benzylideneacetone, phenylacetylene, etc., the reaction is inhibited, and the substrates are reduced.

### Syntheses and Crystal Structures of the Cinchona Alkaloid Derivatives Used as Ligands in the Osmium-Catalyzed Asymmetric Dihydroxylation of Olefins

W. AMBERG, Y. L. BENNANI, R. K. CHADHA, G. A. CRISPINO, W. D. DAVIS, J. HARTUNG, K.-S. JEONG, Y. OGINO, T. SHIBATA and K. B. SHARPLESS, *J. Org. Chem.*, 1993, **58**, (4), 844–849

Ligands of the phthalazine class (DHQ)<sub>2</sub>-PHAL and (DHQD)<sub>2</sub>-PHAL were conveniently synthesised in good yield by the reaction of the corresponding alkaloid with 1,4-dichlorophthalazine in the presence of OsO<sub>4</sub> catalyst, K<sub>2</sub>CO<sub>3</sub> and KOH, in refluxing toluene. Two classes of derivatives of the cinchona alkaloids dihydroquinine and dihydroquinidine were prepared. The alkaloid derivatives act as highly enantioselective ligands for the OsO<sub>4</sub> catalysed asymmetric dihydroxylation of olefins.

### Ruthenium Ammine/Crown Ether Interactions in Solution: Effects of Modification of both Guest and Host on the Strength of Second-Sphere Complexation

M. D. TODD, Y. DONG, J. HORNEY, D. I. YOON and J. T. HUPP, *Inorg. Chem.*, 1993, **32**, (10), 2001–2004

Crown interactions with simple Ru ammine complexes were observed over a range of 10<sup>6</sup> in binding constant with binding being driven by favourable ether O/ammine hydrogen interactions. For hosts, larger binding constants were obtained with larger macrocycles and with more flexible macrocycles. For guests, larger binding constants were observed in higher oxidation states and in the presence of strongly electron-withdrawing ancillary ligands.

### Addition of Carboxylic Acids to Alkynes Catalysed by Ruthenium Complexes

M. ROTEM and Y. SHVO, *J. Organomet. Chem.*, 1993, **448**, (1–2), 189–204

The addition of carboxylic acids to alkynes was catalysed by  $\text{Ru}_3(\text{CO})_{12}$ , as well as by dimeric Ru carboxylate complexes,  $[\text{Ru}(\text{RCOO})(\text{CO})_2(\text{L})_2]_2$ , to yield vinyl esters. A stereospecific kinetically controlled *syn*-addition of the carboxylic acid to the triple bond was observed. The active catalytic species were mononuclear Ru complexes which were also identified as the quenching products.

### Ruthenium-Catalyzed Oxidations for Selective Syntheses of Ketones and Acyl Cyanides. Selective Acylation of Amino Compounds with Acyl Cyanides

S.-I. MURAHASHI and T. NAOTA, *Synthesis*, 1993, (4), 433–440

Studies of the oxidation of alcohols with *tert*-butyl hydroperoxide in the presence of dichlorotris(triphenylphosphine)Ru catalyst yielded corresponding carbonyl compounds with high efficiency. This method can be used for the oxidation of cyanohydrins to give acyl cyanides which are versatile synthetic intermediates. Acylation of amino compounds with acyl cyanides thus obtained proceeds chemoselectively.

## FUEL CELLS

### Influence of Physicochemical Properties on the Performance of Pt/C Porous Electrodes for Oxygen Reduction in Phosphoric Acid

N. GIORDANO, E. PASSALACQUA, P. L. ANTONUCCI, L. PINO, M. VIVALDI, A. PATTI and K. KINOSHITA, *Electrochim. Acta*, 1993, **38**, (7), 913–918

O reduction on Pt/C black in PTFE-bonded porous electrodes in 98%  $\text{H}_3\text{PO}_4$  at 170°C was investigated in ~48 hour long tests. The effect of Pt surface area and volume of acid in the electrode structure (PAO) on the performance of porous electrodes was investigated for Tafel slope, O gain, etc.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Non-Alloyed Ti/Au and Ti/Pt/Au Ohmic Contacts to p-Type InGaAsP

V. MALINA, E. HÁJKOVÁ, J. ZELINKA, M. DAPOR and V. MICHELI, *Thin Solid Films*, 1993, **223**, (1), 146–153

Vacuum evaporated Ti/Au and Ti/Pt/Au metallisations were prepared for non-alloyed ohmic contacts to p-type InGaAsP. The composition and carrier concentration of the quaternary material strongly affected the electrical properties of as-deposited Ti/Au and Ti/Pt/Au contacts. Excellent as-deposited Ti/Au and Ti/Pt/Au low-resistance ohmic contacts were formed with values for the specific contact resistance and for factor  $\eta$  as low as  $1.6 \times 10^{-9} \Omega\text{m}^2$  and 1.4, respectively, when combined with a shallow diffusion of Zn into the 1.3  $\mu\text{m}$  InGaAsP.

### Magneto-Optical Applications of Co/Pt Multilayers

S. HASHIMOTO, A. MAESAKA, K. FUJIMOTO and K. BESSHO, *J. Magn. & Magn. Mater.*, 1993, **121**, (1–3), 471–478

Optimal preparation conditions to achieve low disk noise were studied for Co/Pt multilayers and a SiN underlayer. A 6–8 dB higher carrier-to-noise ratio (CNR) than in TbFeCo disks was achieved at 488 nm. CoNi/Pt multilayers with lower Curie temperature give high write/erase cyclability and high write sensitivity. Recording by magnetic field modulation gave a CNR of 45 dB with a field of 16 kA/m.

### Selective Electroless Ni Deposition onto Pd-Activated Si for Integrated Circuit Fabrication

V. M. DUBIN, S. D. LOPATIN and V. G. SOKOLOV, *Thin Solid Films*, 1993, **226**, (1), 94–98

Selective electroless Ni deposition on Pd-activated Si was studied for the fabrication of a high density and uniform metallisation of complementary metal-oxide-semiconductor devices. X-ray microanalysis of the distribution in NiP/Pd/Si multilayer structure which was obtained by selective electroless NiP deposition on Si with Pd activation after annealing at 400°C in  $\text{N}_2$  showed that the surface resistance of Ni clad polycrystalline Si lines was reduced by a factor of 20.

## MEDICAL USES

### Electrochemical Oxidation of $\text{H}_2\text{O}_2$ on Pt and Pt + Ir Electrodes in Physiological Buffer and Its Applicability to $\text{H}_2\text{O}_2$ -Based Biosensors

Y. ZHANG and G. S. WILSON, *J. Electroanal. Chem.*, 1993, **345**, (1 and 2), 253–271

The electrochemical oxidation of  $\text{H}_2\text{O}_2$  on Pt disk and Pt + Ir wire electrodes was studied in physiological buffer at pH 7.4. The electrode reaction was a two-electron irreversible process. The oxidation of  $\text{H}_2\text{O}_2$  is concentration dependent, but is  $\text{O}_2$  pressure independent at low  $\text{H}_2\text{O}_2$  concentration. The detection of  $\text{H}_2\text{O}_2$  is strongly affected by pH, temperature and electrode surface conditioning. An oxidised surface is needed to obtain a stable  $\text{H}_2\text{O}_2$  response and reductive pretreatment of the electrode always yields prolonged stabilisation times.

### Preparation, Characterization, and Antitumor Activity of New Ethylenediamine Platinum(IV) Complexes Containing Mixed Carboxylate Ligands

A. R. KHOKHAR, Y. DENG, Y. KIDO and Z. H. SIDDIK, *J. Inorg. Biochem.*, 1993, **50**, (2), 79–87

New potentially useful ethylenediamine Pt(IV) analogues containing carboxylate ligands in the axial and equatorial positions were synthesised and characterised. Carboxylate groups in the axial position have a substantial influence on antitumour activity for equatorial monodentate bis-carboxylato analogues, but less influence for bidentate carboxylato analogues. Complexes with axial trifluoroacetate and equatorial monodentate carboxylate ligands are very promising.