

# ABSTRACTS

of current literature on the platinum metals and their alloys

## PROPERTIES

### Properties of PdCu(110) Single Crystal Alloy Surfaces: Temperature-Induced Processes in the Surface Microstructure

J. LOBODA-CACKOVIC, *Vacuum*, 1996, 47, (12), 1405–1411

PdCu(110) alloy single crystal surfaces, with atomic concentration ratio Cu:Pd of 1:1 in the bulk, were prepared with a Cu:Pd ratio of 0.3–2 in the ~4 layers deep, surface region. The PdCu(110) surface consists of small crystalline domains containing ~10–20 lattice cells depending on preparation. Two temperature-induced surface processes change the surface microstructure: surface roughening and partial surface disordering, starting at ~550 and ~700 K, respectively.

### Study of the Reactions $\Gamma + \text{IrCl}_6^{2-}$ and $\text{Fe}(\text{CN})_6^{4-} + \text{S}_2\text{O}_8^{2-}$ in Micellar Solutions

R. JIMÉNEZ, M. M. GRACIANI, A. RODRÍGUEZ, M. L. MOYÁ, F. SÁNCHEZ and P. LÓPEZ-CORNEJO, *Langmuir*, 1997, 13, (2), 187–191

The kinetics of the reactions  $\Gamma + \text{IrCl}_6^{2-}$  and  $\text{Fe}(\text{CN})_6^{4-} + \text{S}_2\text{O}_8^{2-}$  were studied in anionic micelles of Na dodecylsulfate at 298.2 K. The present work and the results in Na bis-2-ethylhexyl sulfosuccinate/decane/ $\text{H}_2\text{O}$  microemulsions and aqueous Na nitrate were explained by using as a starting point the Brønsted equation.

## CHEMICAL COMPOUNDS

### Chloride Anion Recognition by Neutral Platinum(II) and Palladium(II) 5,5'-bis-amide Substituted Bipyridyl Receptor Molecules

P. D. BEER, N. C. FLETCHER, M. G. B. DREW and T. J. WEAR, *Polyhedron*, 1997, 16, (5), 815–823

A series of new acyclic neutral Pt(II) and Pd(II) 5,5'-bis-amide substituted 2,2'-bipyridyl receptors have been synthesised and the X-ray structures of two receptors determined. Proton NMR anion binding studies in deuterated dimethylsulfoxide solution reveal that these neutral receptors complex the halide anion via favourable amide  $\text{CO}-\text{NH} \cdots \text{Cl}^-$  H bonding interactions.

### Self-Assembly of Tetraalkylammonium Salt-Stabilized Giant Palladium Clusters on Surfaces

M. T. REETZ, M. WINTER and B. TESCHE, *Chem. Commun.*, 1997, (2), 147–148

Nanostructural Pd clusters, stabilised by a monomolecular coat of surfactants  $\text{N}(\text{C}_8\text{H}_{17})_4\text{Br}$  or  $\text{N}(\text{C}_{18}\text{H}_{37})_4\text{Br}$ , self-assembled on C surfaces in an ordered manner to form h.c.p. structures. These structures self-organised into two-dimensional films and three-dimensional superlattices, controlled by varying the length of the alkyl chains on the ammonium ions.

### Synthesis and Structural Characterisation of $[\text{Pd}_2(\mu\text{-Br})_2(\text{PBu}_3)_2]$ , an Example of a Palladium(I)-Palladium(I) Dimer

R. VILAR, D. M. P. MINGOS and C. J. CARDIN, *J. Chem. Soc., Dalton Trans.*, 1996, (23), 4313–4314

The synthesis, spectroscopic characterisation and, when  $\text{X} = \text{Br}$ , the single-crystal structure, of the novel Pd'-Pd' dimers  $[\text{Pd}_2(\mu\text{-X})_2(\text{PBu}_3)_2]$  ( $\text{X} = \text{Br}$  or  $\text{I}$ ) are described. Preliminary results on their reactions with  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{CNC}_6\text{H}_5\text{Me}_2$  and  $\text{C}_2\text{H}_2$  are also reported. When dissolved in toluene,  $[\text{Pd}_2(\mu\text{-X})_2(\text{PBu}_3)_2]$  were good initiators for the polymerisation of acetylene; with  $\text{X} = \text{I}$  the dimer was catalytic.

### Formation of Zerovalent Palladium from the Cationic Complex $\text{Pd}(\text{PPh}_3)_2(\text{BF}_4)_2$ in the Presence of PPh<sub>3</sub> and Water in DMF

C. AMATORE, A. JUTAND and M. J. MEDEIROS, *New J. Chem.*, 1996, 20, (11), 1143–1148

Stable Pd(0) complexes were spontaneously and slowly generated *in situ* from the cationic Pd(II) complex  $\text{Pd}(\text{PPh}_3)_2(\text{BF}_4)_2$  in the presence of triphenylphosphine ( $\text{PPh}_3$ ) and  $\text{H}_2\text{O}$ . The generated ( $\text{PPh}_3$ ) oxide shows that ( $\text{PPh}_3$ ) can reduce the Pd(II) to Pd(0), probably via a Pd(II) hydroxy-containing intermediate.

### Large Second-Order Nonlinear Optical Properties of Novel Organometallic ( $\sigma$ -Aryl-enynyl)Ruthenium Complexes

S. HOUBRECHTS, K. CLAYS, A. PERSOONS, V. CADIerno, M. P. GAMASA and J. GIMENO, *Organometallics*, 1996, 15, (25), 5266–5268

A series of novel Ru  $\sigma$ -acceptor aryl-enynyl complexes, including homo- and heterobimetallic complexes, have been synthesised and their nonlinear properties evaluated. The effects upon the hyperpolarisability of chain length, configuration of the metal donor group, and nature of the metal acceptor group are reported. These complexes are found to possess the largest quadratic hyperpolarisabilities, reported to date, for bimetallic compounds.

### A Novel Route to Butatrienyliene Complexes: Stabilisation of $:\text{C}=\text{C}=\text{CH}_2$ on Ru<sub>5</sub> Clusters

C. J. ADAMS, M. I. BRUCE, B. W. SKELTON and A. H. WHITE, *Chem. Commun.*, 1996, (23), 2663–2664

The addition of  $\text{C}_2(\text{SiMe}_3)_2$  to  $[\text{Ru}_5(\mu_5\text{-C}_2)(\mu\text{-PPh}_2)_2(\mu\text{-SMe})_2(\text{CO})_{11}]$  gave  $[\text{Ru}_5\{\mu_4\text{-CCCCCH}(\text{SiMe}_3)\}(\mu\text{-PPh}_2)_2(\mu\text{-SMe})(\mu_3\text{-SMe})(\text{CO})_{10}]$  (1) as a mixture of geometrical isomers in 94% yield. Alkaline hydrolysis of (1) resulted in the first stable butatrienyliene complex  $[\text{Ru}_5(\mu_4\text{-CCCCCH}_2)(\mu\text{-PPh}_2)_2(\mu\text{-SMe})(\mu_3\text{-SMe})(\text{CO})_{10}]$  (2) in 84% yield. The spiked-rhomboidal pentanuclear complex  $[\text{Ru}_5(\mu_4\text{-CCCCCH}_2)(\mu\text{-PPh}_2)_2(\mu\text{-SMe})_2(\text{CO})_{11}]$  was isolated in 62% yield from the carbonylation of (2).

## Synthetic, Structural, Electrochemical and Electronic Characterisation of Heterobimetallic bis(acetylide) Ferrocene Complexes

M. C. B. COLBERT, J. LEWIS, N. J. LONG, P. R. RAITHBY, A. J. P. WHITE and D. J. WILLIAMS, *J. Chem. Soc., Dalton Trans.*, 1997, (1), 99–104

A series of novel heterobimetallic bis(acetylide) ferrocene complexes of the form  $[(C_5H_5)Fe^{II}(C_5H_4)C\equiv CRu^{II}(dppm)_2(C\equiv CR)]$  ( $dppm = 1,2$ -bis(diphenylphosphino)methane) are reported. Incorporation of donor-substituted aromatic acetylide ligands causes a cathodic shift in the  $Ru^{II/III}$  redox potential, while electron-withdrawing substituents lead to an anodic shift. The structure of *trans*- $[Ru(dppm)_2\{C\equiv C(C_6H_4)-Fe(C_6H_5)\}_2]$  shows the Ru centre linearly bound to 2 ferrocene units by rigid rod-like acetylene linkages.

## Thermal Decomposition of the bis(dihydrogen) Complex $RuH_2(H_2)_2(PCy_3)_2$ in the Solid State

B. CHAUDRET, P. DAGNAC, D. LABROUE and S. SABOETIENNE, *New J. Chem.*, 1996, 20, (11), 1137–1141  
Temperature programmed decomposition studies of  $RuH_2(H_2)_2(PCy_3)_2$  (1) were performed under a flow of He. Study of the  $H_2$  evolution revealed a two-step process. In the first step, (1) was reversibly transformed into a mixture of  $RuH_3[(\eta^1-C_6H_5)PCy_3]$  ( $PCy_3$ ) and  $RuH(\eta^1-C_6H_5)PCy_3[(\eta^2-C_6H_5)PCy_3]$ . In the second step,  $C_6H_5$  was lost and the Ru complexes transformed into unidentified species. Under  $H_2$ ,  $C_6H_5$  was converted into cyclohexane, thus demonstrating the catalytic properties of the Ru complexes.

## Temperature Independent Ru $\rightarrow$ Os Electronic Energy Transfer in a Rodlike Dinuclear Complex with a 2.4 nm Intermetal Separation

L. HAMMARSTRÖM, F. BARIGELLETTI, L. FLAMIGNI, N. ARMAROLI, A. SOUR, J.-P. COLLIN and J.-P. SAUVAGE, *J. Am. Chem. Soc.*, 1996, 118, (47), 11972–11973

Energy transfer is studied in a rodlike dinuclear complex,  $(tpp)Ru(tpy-ph-bco-ph-tpy)Os(tpp)^{II+}$  ( $tpy = 2,2':6',2''$ -terpyridine,  $tpp = 4'$ -*p*-tolyl-*tpy*,  $ph = 1,4$ -phenylene and  $bco = bicyclo[2.2.2]octane$ ), which has a rigid, linear geometry. The  $Ru \rightarrow Os$  energy transfer rate was found to be  $5.2 \times 10^8 s^{-1}$  ( $\pm 20\%$ ) at 90–200 K. Energy transfer is therefore unaffected by the temperature changes and state of the solvent.

## ELECTROCHEMISTRY

### Kinetic Study of the Hydrogen Oxidation Reaction on Platinum and Nafion® Covered Platinum Electrodes

R. M. Q. MELLO and E. A. TICIANELLI, *Electrochim. Acta*, 1997, 42, (6), 1031–1039

Hydrogen oxidation at Pt and Pt/polymer electrolyte interfaces in contact with solutions of  $H_2SO_4$  and  $K_2SO_4$  at pH 0.2–7.5 was studied using cyclic voltammetry, rotating disk electrode and potential step chronoamperometry. The solubility and the diffusion coefficient of  $H_2$  gas in the solutions and the permeability in the polymer electrolyte were determined.

## Electrocrystallization of a Halogen-Bridged Mixed-Valence Platinum Complex

H. AWANO, T. KUMAZAWA and K. KASUYA, *Electrochim. Acta*, 1997, 42, (3), 483–488

Electrocrystallisation of  $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$  (1), a halogen-bridged mixed-valence Pt complex with  $Pt^{II}\cdots X-Pt^{IV}\cdots X\cdots$  chains, is reported. Electrochemical reduction of *trans*- $[PtCl_2(en)_2]Cl_2$  in a solution of perchloric acid at  $-1.5$  to  $-1.6$  V vs. a Pt counter electrode gave red needle crystals of (1) several mm long, on a Sn-doped In oxide substrate. No crystals formed during electrochemical oxidation of a  $Pt^{II}$  complex.

## On the Nature of the Interaction of $H_2PdCl_4$ with the Surface of Graphite-Like Carbon Materials

P. A. SIMONOV, A. V. ROMANENKO, I. P. PROSVIRIN, E. M. MOROZ, A. I. BORONIN, A. L. CHUVILIN and V. A. LIKHOLOBOV, *Carbon*, 1997, 35, (1), 73–82

The adsorption of  $H_2PdCl_4$  from aqueous solutions onto the surface of graphite-like C materials proceeded through two competitive pathways: (1) reduction, giving rise to  $Pd^0$  particles of 6–100 nm in size localised near the exterior surface of the porous C particles and (2) formation of  $\pi$ -complexes of  $PdCl_2$  with  $>C=C<$  fragments of the C matrix, which takes place on the whole surface of the particles. The ratio, dispersion and morphology of the adsorbed  $Pd^{2+}$  and  $Pd^0$  species are found to be dependent upon many factors.

## Effect of a Graphite Pad on the Adsorption and the Electrocatalytic Activity of Microdeposits of Rhodium

E. HOROZOVA, Z. JORDANOVA and M. VELKOV, *Electrochim. Acta*, 1997, 42, (3), 369–376

The effect of a graphite pad on the adsorption and electrocatalytic activity of Rh microdeposits electrochemically dispersed on graphite was studied with regard to  $H_2$  and electrocatalysis towards cathodic  $H_2$  evolution. The type of graphite affects adsorptivity and the energy spectrum of  $H_2$  adsorption, and has some effect on the specific currents and kinetic parameters of the cathodic liberation of  $H_2$ . Electron microscopic studies of rhodanised graphite electrodes showed that the role of the graphite pad is in the formation of Rh deposits of different structure.

## Supramolecular Electrode Materials Derived from Pyrrole-Substituted Ruthenium(II) Bipyridyl Calix[4]arenes

H. C.-Y. BETTEGA, M. HISSLER, J.-C. MOUTET and R. ZIESSEL, *Chem. Mater.*, 1997, 9, (1), 3–5

Electropolymerisation of calixarenes bearing pendant Ru complexes, to produce poly(calixarene- $[Ru(bpy)_3]^{2+}$ ) ( $bpy = 2,2'$ -bipyridine)(1) modified electrodes is reported. Pyrrole-substituted (1) were prepared by heating the bipyridyl mono- and disubstituted calixarenes with  $Ru(L)_2Cl_2$  ( $L = 4$ -(pyrrol-1-yl)-4'-methyl-2,2'-bipyridine) at  $60^\circ C$  in EtOH, followed by precipitation as hexafluorophosphate salts. Electrodes were coated by oxidative homo- and copolymerisation, with *N*-methylpyrrole, of the monomer complexes.

## PHOTOCONVERSION

### Photocatalytic Transfer Hydrogenation of Schiff Bases with Propan-2-ol by Suspended Semiconductor Particles Loaded with Platinum Deposits

B. OHTANI, Y. GOTO, S.-I. NISHIMOTO and T. INUI, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, (21), 4291–4295  
Photoirradiation at >300 nm of a propan-2-ol solution of Schiff bases (*N*-benzylidenebenzylamine and *N*-benzylideneaniline) containing platinumised TiO<sub>2</sub> (TiO<sub>2</sub>-Pt), or CdS loaded with PtO<sub>2</sub>, gave the corresponding secondary amines (dibenzylamine and *N*-benzylamine, respectively) via catalytic transfer hydrogenation. The most efficient catalyst has small Pt deposits dispersed uniformly on each TiO<sub>2</sub> particle.

### Photocatalytic Hydrogen Production by Dye-Sensitized Pt/SnO<sub>2</sub> and Pt/SnO<sub>2</sub>/RuO<sub>2</sub> in Aqueous Methyl Viologen Solution

K. GURUNATHAN, P. MARUTHAMUTHU and M. V. C. SASTRI, *Int. J. Hydrogen Energy*, 1997, **22**, (1), 57–62  
H<sub>2</sub> photoproduction by a wide band gap SnO<sub>2</sub> semiconductor in powder form loaded with Pt and RuO<sub>2</sub>, and sensitised by Ru(bpy)<sub>3</sub><sup>2+</sup> and organic dyes or with low band gap CdS semiconductor, was studied. Acriflavin, Eosin Blue, Rhodamine B, Rose Bengal and Fluorescein were used as photosensitisers in the presence of methyl viologen (MV<sup>2+</sup>), with or without EDTA as a sacrificial agent. The maximum rate of H<sub>2</sub> production was observed at [Ru(bpy)<sub>3</sub><sup>2+</sup>] = 3.75 × 10<sup>-5</sup> mol dm<sup>-3</sup> and [MV<sup>2+</sup>] = 2.5 × 10<sup>-3</sup> mol dm<sup>-3</sup>.

### Femtosecond Dynamics of Excited-State Evolution in [Ru(bpy)<sub>3</sub>]<sup>2+</sup>

N. H. DAMRAUER, G. CERULLO, A. YEH, T. R. BOUSSIE, C. V. SHANK and J. K. MCCUSKER, *Science*, 1997, **275**, (5296), 54–57

The earliest events associated with excited-state relaxation in tris(2,2'-bipyridine)Ru(II) were monitored by time-resolved absorption spectroscopy on the femtosecond time scale. The data revealed dynamics associated with the temporal evolution of the Franck-Condon state to the lowest energy excited state of this molecule, which was completed in ~ 300 femtoseconds after the initial excitation.

### Hydrogen Generation Using Water-Insoluble Polymer-Bound Ruthenium(II) Complexes

M. SUZUKI, S. KOBAYASHI, M. KIMURA, K. HANABUSA and H. SHIRAI, *Chem. Commun.*, 1997, (2), 227–228

Water-insoluble free-standing films of partially quaternised poly(1-vinylimidazole)-bound Ru(II) complexes were prepared and used as polymer-solid photosensitisers for H<sub>2</sub> generation. When an aqueous solution containing the polymer-bound Ru(II) complex film, methyl viologen (MV<sup>2+</sup>), triethanolamine and bis(2,2'-bipyridine)Pt(II) was irradiated with light ( $\lambda$  > 440 nm) H<sub>2</sub> was generated. Electron transfer from the photoexcited Ru(II) complex to the MV<sup>2+</sup> species on the polymer surface forms MV<sup>•+</sup> species which diffuse into the bulk solution and react with Pt giving H<sub>2</sub>.

### Excited State Properties of bis-Tetraaza-phenanthrene-Ru(II) Diad Complexes with a Ferrocenyl Unit

S. CHOUA, A. KIRSCH-DE MESMAEKER, L. JACQUET, C. MARZIN and N. CHABERT, *J. Photochem. Photobiol., A: Chem.*, 1996, **99**, (2-3), 127–136

The excited state properties of the diad complexes Ru(tap)<sub>2</sub>(ppFc)<sup>2+</sup> and Ru(bpy)<sub>2</sub>(ppFc)<sup>2+</sup> (tap = 1,4,5,8-tetraazaphenanthrene and bpy = 2,2'-bipyridine), bearing a reducing ferrocenyl (Fc) centre on a derivatised (pyridine)pyrazole (pp) ligand, were compared with those of the corresponding complexes lacking a Fc unit. Intermolecular photoelectron transfer with ferrocene was favoured when bpy was replaced by tap. The different excited state behaviour in the absence of reducing agent was explained on the basis of photophysical data available for other tap complexes.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Epitaxial Growth of Thin Films of SrTi<sub>1-x</sub>Ru<sub>x</sub>O<sub>3-y</sub> by Pulsed Laser Deposition

A. GUPTA, B. W. HUSSEY and T. M. SHAW, *Mater. Res. Bull.*, 1996, **31**, (12), 1463–1470

Pulsed laser deposition is used to epitaxially grow SrTi<sub>1-x</sub>Ru<sub>x</sub>O<sub>3-y</sub> (0 ≤ x ≤ 1) thin films on (100)-orientated SrTiO<sub>3</sub> substrates. The films are grown in a low pressure O<sub>2</sub> ambient with *in situ* characterisation of the surface using RHEED. The solid solution films are potentially useful as lattice-matched buffer layers for heteroepitaxial growth, or as barrier layers in tunnel junctions with controlled resistive properties.

## APPARATUS AND TECHNIQUE

### Amperometric Determination of Nitrite via Reaction with Iodide Using Microelectrodes

M. BERTOTTI and D. PLETCHER, *Anal. Chim. Acta*, 1997, **337**, (1), 49–55

The measurement of steady state currents at Pt microdisk electrodes (radii 2.5–10 μm), generated from the quantitative conversion of iodide to triiodide by nitrite in 0.1 M H<sub>2</sub>SO<sub>4</sub>, is the basis of a method for the determination of nitrite in H<sub>2</sub>O. This rapid and simple procedure can be used to reliably determine levels ≥ 0.1 μM in natural H<sub>2</sub>O and human saliva.

### Glucose Detection at Bare and Sputtered Platinum Electrodes Coated with Polypyrrole and Glucose Oxidase

P. J. H. J. VAN OS, A. BULT, C. G. J. KOOPAL and W. P. VAN BENNEKOM, *Anal. Chim. Acta*, 1996, **335**, (3), 209–216

Glucose sensors have been fabricated by the galvanostatic polymerisation of 0.3 M pyrrole in 4-(2-hydroxyethyl)-1-piperazine-ethane sulfonic acid buffer (pH 7.0) with 200 U ml<sup>-1</sup> glucose oxidase using a current of 1 μA at bare and sputtered Pt electrodes. Addition of flavine adenine dinucleotide did not increase the glucose response. The selectivity for other sugars (lactose, galactose and fructose) was good.

## Development of a Novel Manganese Oxide-Clay Humidity Sensor

K. MIYAZAKI, M. HIEDA and T. KATO, *Ind. Eng. Chem. Res.*, 1997, **36**, (1), 88–91

Clay materials, such as kaolinite (1), muscovite (2), etc., were used as components in a potential-type humidity sensor, Pt/EMD/M, where EMD is electrolytic MnO<sub>2</sub>, and M is Cu or Al. With (1) and (2), the humidity-sensing characteristics of EMD were enhanced, giving good linearity and fast response. A mechanism for this enhancement was proposed, based on the role of inter-layer H<sub>2</sub>O molecules in the EMD-additive system.

## Fluorescence-Based Thin Plastic Film Ion-Pair Sensors for Oxygen

A. MILLS and M. THOMAS, *Analyst*, 1997, **122**, (1), 63–68

Thin-film sensors for O<sub>2</sub>, which incorporate the dye ion-pair, tris(4,7-diphenyl-1,10-phenanthroline) Ru(II) ditetraphenylborate in a variety of thin film polymer/plasticiser matrices, have been prepared. When poly(methyl methacrylate) was used as the polymer and tri-*n*-butyl phosphate as the plasticiser, the sensitivity of the film towards O<sub>2</sub> increased markedly with increasing level of the plasticiser, but was largely independent of temperature and age. An O<sub>2</sub> sensor exposed to alternating O<sub>2</sub> and N<sub>2</sub> showed a 0–90% response and recovery times of 0.4 and 4.4 s, respectively.

## HETEROGENEOUS CATALYSIS

### Transient and Resonant Behavior for NO Reduction by CO over a Pt/Al<sub>2</sub>O<sub>3</sub> Catalyst during Forced Composition Cycling

R. R. SADHANKAR and D. T. LYNCH, *Can. J. Chem. Eng.*, 1996, **74**, (5), 674–682

The reduction of NO by CO over a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst was studied in an isothermal recycle reactor at 485 K. Maximum time-average CO and NO conversions of 66 and 78%, respectively, were achieved from out-of-phase feed concentration cycling at a frequency of 5.5 mHz, compared with the steady-state conversions of 2 and 3.8%, respectively. The difference in the CO and NO conversions was due to the formation of N<sub>2</sub>O. Higher NO conversions were obtained by decreasing the NO phase lead to below 180°.

### Catalytic Testing of TiO<sub>2</sub>/Platinum/Silicalite-1 Composites

N. VAN DER PUIL, E. J. CREYGHTON, E. C. RODENBURG, T. S. SIE, H. VAN BEKKUM and J. C. JANSEN, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, (22), 4609–4615

The synthesis, characterisation and testing of composite TiO<sub>2</sub>-supported Pt catalyst particles, covered with a 0.8–1.3 μm thick silicalite-1 layer, are described. The composite shows mass transport selectivity giving high ratios of the initial conversion rates (35 at 100°C) in the competitive hydrogenation of a linear and a dibranched alkene. Steric constraints observed at the catalytic sites lead to regioselectivity in the hydrogenation of long-chain alkenes. A linear alkene with a terminal double bond is converted preferentially over an isomer with an internal double bond.

## Hydrodesulfurization over PdMo/HY Zeolite Catalysts

B. PAWELEC, R. NAVARRO, J. L. G. FIERRO, J. F. CAMBRA, F. ZUGAZAGA, M. B. GÜEMEZ and P. L. ARIAS, *Fuel*, 1997, **76**, (1), 61–71

A series of binary PdMo/HY zeolite catalysts has been prepared by a two-step impregnation procedure and tested in the hydrodesulfurisation (HDS) of dibenzothiophene and diesel oil (1.1 wt.% S). Pd/HY was more active than PdMo/HY, suggesting an inhibitory effect of Mo on activity, due to the formation of H<sub>2</sub>MoS<sub>2</sub> and S[PdH<sup>+</sup>] hydride-type sulfides in the PdMo zeolites. The initial S conversion in HDS of gas oil over Pd/HY was similar to that on a CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst, but both Pd/HY catalyst and the blank HY zeolite deactivated rapidly at short times on-stream.

## The Semihydrogenation of Acetylenes over Pd Catalyst on BER in the Presence of CsI

N. M. YOON, K. B. PARK, H. J. LEE and J. CHOI, *Tetrahedron Lett.*, 1996, **37**, (47), 8527–8528

Pd(OAc)<sub>2</sub> on borohydride exchange resin (BER) in 95% ethanol, in the presence of CsI, was found to be a highly selective catalyst for the semihydrogenation of acetylenes. Terminal acetylenes were converted to the corresponding terminal olefins and internal acetylenes to the corresponding *cis*-olefins in virtually quantitative yield at room temperature.

## Polymer-Supported Palladium and Rhodium Species as Hydrogenation Catalysts

P. C. SELVARAJ and V. MAHADEVAN, *J. Polymer Sci., A: Polymer Chem.*, 1997, **35**, (1), 105–122

New copolymers containing amino and heterocyclic ligands were prepared and used to anchor Pd(OAc)<sub>2</sub> and RhCl<sub>3</sub>.xH<sub>2</sub>O to give highly active catalysts for the hydrogenation of alkenes, dienes, alkynes and nitrobenzene under very mild conditions. Relative reactivities and the effects of substrate structure, solvents, catalyst loading, anchoring ligands, metal species and particle size on the hydrogenation rates were determined. Recycling efficiencies of the catalysts were very good.

## Fullerene-Based Ruthenium Catalysts: A Novel Approach for Anchoring Metal to Carbonaceous Supports. I. Structure. II. Hydrogenation Activity

T. BRAUN, M. WOHLERS, T. BELZ, G. NOWITZKE, G. WORTMANN, Y. UCHIDA, N. PFÄNDER and R. SCHLÖGL, *Catal. Lett.*, 1997, **43**, (3, 4), 167–173; 175–180

The effect of fullerenes and related carbonaceous support materials on the structural and catalytic properties of Ru was studied. Catalysts based on C<sub>60</sub>, raw fullerene black, extracted fullerene black, cathode deposit and graphite were prepared by a combined impregnation/activation reaction based on the thermally induced decomposition of Ru<sub>3</sub>(CO)<sub>12</sub>. The catalysts were studied using low-temperature CO hydrogenation and liquid-phase hydrogenation of 2-cyclohexenone. The role of non-six-membered C rings in the support materials on the stability and catalytic performance of the Ru particles is discussed.

## Ruthenium Porphyrin Encapsulated in Modified Mesoporous Molecular Sieve MCM-41 for Alkene Oxidation

C.-J. LIU, S.-G. LI, W.-Q. PANG and C.-M. CHE, *Chem. Commun.*, 1997, (1), 65–66

[RuL(CO)(EtOH)] (where H<sub>2</sub>L is *meso*-tetrakis(4-chlorophenyl)porphyrin) encapsulated in MCM-41, modified with 3-aminopropyltriethoxysilane, is reported as a stable catalyst for the oxidation of alkenes by *tert*-butyl hydroperoxide. When 0.1 wt.% Ru/MCM-41 catalyst was used, significantly higher turnovers and longer catalyst lifetimes were achieved for a range of alkenes, than with free [RuL(CO)(EtOH)].

## The Nature of Ruthenium Sulfide Clusters Encaged in a Y Zeolite

B. MORAWECK, G. BERGERET, M. CATTENOT, V. KOUKIONAS, C. GEANTET, J.-L. PORTEFAIX, J. L. ZOTIN and M. BREYSSE, *J. Catal.*, 1997, 165, (1), 45–56

Catalysts of RuS<sub>2</sub> supported in a dealuminated KY zeolite were prepared by ion exchange and subsequent sulfidation by H<sub>2</sub>S/H<sub>2</sub>. They were characterised by HREM, EDX, TPR and EXAFS. The activity for the hydrogenation of tetralin, carried out in the presence of excess H<sub>2</sub>S (1.85%), was very high and roughly 300 times that (expressed per metal atom) of an industrial NiMo/Al<sub>2</sub>O<sub>3</sub> hydrotreating catalyst. The active phase was found to consist of clusters of < 50 Ru atoms of a RuS<sub>2</sub>-like phase with very small domains of Ru metal.

## HOMOGENEOUS CATALYSIS

### Hydration of Alkynes by a PtCl<sub>2</sub>-CO Catalyst

W. BAIDOSI, M. LAHAV and J. BLUM, *J. Org. Chem.*, 1997, 62, (3), 669–672

The treatment of PtCl<sub>2</sub> with CO at 40–110°C forms a HPtCl(CO)<sub>2</sub> complex, which acts as a highly efficient and selective catalyst for the hydration of aliphatic and aromatic acetylenes. The catalyst operates both under homogeneous conditions in wet THF and under phase-transfer conditions in (CHCl<sub>2</sub>)<sub>2</sub>/H<sub>2</sub>O in the presence of tricaprylmethylammonium chloride (Aliquat 336). This system is more environmentally friendly than the conventionally used Hg-based process and more efficient than other transition metal-catalysed processes.

### Chirality Transfer via the Palladium-Catalyzed Cross-Coupling Reaction of Optically Active 2-Cyclohexenylsilane: Stereochemical and Mechanistic Aspects

T. HIYAMA, H. MATSUHASHI, A. FUJITA, M. TANAKA, K. HIRABAYASHI, M. SHIMIZU and A. MORI, *Organometallics*, 1996, 15, (26), 5762–5765

The cross-coupling of the optically active silane (*S*)-(2-cyclohexenyl)difluorophenylsilane (1) with aryl halide or triflate, catalysed by Pd(PPh<sub>3</sub>)<sub>4</sub>, in the presence of fluoride ion proceeds stereospecifically, strongly depending upon the nature of the reactants. The reaction of (1) with 4-iodoacetophenone and tetrabutylammonium fluoride gave the product with retention of configuration, but the reaction with the corresponding triflate using CsF gave the inversion product.

## Palladium-Catalyzed Additions of Terminal Alkynes to Acceptor Alkynes

B. M. TROST, M. T. SORUM, C. CHAN, A. E. HARMS and G. RÜHTER, *J. Am. Chem. Soc.*, 1997, 119, (4), 698–708

The addition of the C–H bond of terminal alkynes to either terminal alkynes (self-coupling) or activated internal alkynes (cross-coupling) to produce conjugated enynes, in the presence of a catalytic amount of Pd acetate and the electron-rich sterically encumbered ligand, tris(2,6-dimethoxyphenyl)phosphine, is reported. This system gives excellent yields of both 1:1 homo- and cross-coupled products. The extraordinary chemoselectivity suggests that any functionality will be compatible with this reaction. The chemoselectivity and excellent regio- and diastereoselectivity make this a very valuable reaction in organic synthesis.

## A New Approach to the Solid-Phase Suzuki Coupling Reaction

S. R. PIETTRE and S. BALTZER, *Tetrahedron Lett.*, 1997, 38, (7), 1197–1200

The reaction of polymer-bound aryl halides with a pinacol ester of diboron under a catalytic Pd(0) system gave the corresponding polymer-bound boronates. The Suzuki coupling reaction was then carried out with a variety of aryl halides under the most efficient system, Pd(PPh<sub>3</sub>)<sub>4</sub>/K<sub>3</sub>PO<sub>4</sub>/DMF, at 80°C. Cleavage from the support with trifluoroacetic acid gave the expected products in unusually good yields and with high purity (> 98%).

## RhCl(PPh<sub>3</sub>)<sub>3</sub> and RhH(PPh<sub>3</sub>)<sub>4</sub> Catalyzed Hydrogenation of Acrylonitrile-Butadiene Copolymers

J. S. PARENT, N. T. MCMANUS and G. L. REMPEL, *Ind. Eng. Chem. Res.*, 1996, 35, (12), 4417–4423

Both RhCl(PPh<sub>3</sub>)<sub>3</sub> (1) and RhH(PPh<sub>3</sub>)<sub>4</sub> (2) are efficient catalytic systems for the selective hydrogenation of acrylonitrile-butadiene copolymers under severe reaction conditions. Detailed kinetic and selectivity data and the effect of varying process conditions upon the rate of hydrogenation are reported. Dilute solution viscosity data are used to show the uniform selectivity of (1) and (2) catalysed hydrogenations. A probable reaction mechanism for the RhCl(PPh<sub>3</sub>)<sub>3</sub> system was derived using analysis of variance model discrimination procedures.

## Isomerization of Hexene Using Dihydridorhodium Complex in Dimethyl Sulfoxide

N. KAMEDA and R. SANGO, *Nippon Kagaku Kaishi*, 1996, (12), 1014–1018

The isomerisation of 1-hexene with a dihydrido(1,3-diphenyltriazenido)bis(triphenylphosphine)Rh(III) (dihydridoRh complex)-dimethyl sulfoxide system was studied under 1 atm pressure of H<sub>2</sub> or N<sub>2</sub> at 30°C. Under H<sub>2</sub>, the isomerisation and hydrogenation of 1-hexene decreased in the order: *trans*-2-hexene > *cis*-2-hexene > hexane, whereas under N<sub>2</sub>, isomerisation was slower and the reaction products were initially found to be in the order: *cis*-2-hexene > *trans*-2-hexene.

### Phosphoramidites: Novel Modifying Ligands in Rhodium Catalysed Hydroformylation

A. VAN ROOY, D. BURGERS, P. C. J. KAMER and P. W. N. M. VAN LEEUWEN, *Recl. Trav. Chim. Pays-Bas*, 1996, **115**, (11/12), 492–498

Several monodentate and bidentate phosphoramidites were prepared and tested as ligands in the hydroformylation of oct-1-ene and styrene using  $\text{Rh}(\text{CO})_2\text{Acac}$  as catalyst precursor. The monodentate ligands are probably too bulky to give satisfactory results. The diphosphoramidite ligands, especially those that co-ordinate bis-equatorially in the trigonal bipyramidal Rh complexes, give hydroformylation catalysts with good rates and selectivities. With modification, chiral phosphoramidites can be readily obtained, which may be suitable for enantioselective catalysis.

### Hydroformylation of 2,4,4-Trimethyl-1-pentene Catalyzed by the High Nuclearity Carbonyl Cluster $[\text{Rh}_{12}(\text{CO})_{30}]^2$

R. DELLA PERGOLA, L. GARLASCHELLI, S. MARTINENGO and A. REPOSSI, *J. Mol. Catal. A: Chem.*, 1997, **115**, (2), 265–271

The hydroformylation of 2,4,4-trimethyl-1-pentene in tetrahydrofuran was catalysed by the precursor  $\text{Na}_2[\text{Rh}_{12}(\text{CO})_{30}]$ , which readily fragmented to give derivatives of lower nuclearity, under high pressures of  $\text{CO}/\text{H}_2$  (20–120 atm) at 300–400 K. The reaction is highly chemioselective, approaching 100% selectivity to 3,5,5-trimethylhexanal. Typical turnover numbers are 100–1000 mol olefin/mol cluster. The order of the reaction with CO was positive.

### A Novel Water-Soluble Rhodium-Poly(enolate-co-vinyl alcohol-co-vinyl acetate) Catalyst for the Hydroformylation of Olefins

J. CHEN and H. ALPER, *J. Am. Chem. Soc.*, 1997, **119**, (5), 893–895

The water-soluble polymer, poly(enolate-co-vinyl alcohol-co-vinyl acetate) (PEVV) is reported as a valuable ligand for the Rh biphasic catalytic hydroformylation of olefins, especially aliphatic olefins. The average turnover frequency for the catalytic hydroformylation of 1-octene was  $5.46 \times 10^5 \text{ kmol} (\text{kg}(\text{Rh})\text{s})^{-1}$  at 90°C and of 1-dodecene was  $2.36 \times 10^4 \text{ kmol} (\text{kg}(\text{Rh})\text{s})^{-1}$  at 60°C. Selective hydroformylation of styrene and its derivatives gave up to 97% of branched-chain aldehyde using Rh-PEVV under biphasic reaction conditions but at low conversions.

### Catalytic Dehydrogenation of Cycloalkanes to Arenes by a Dihydrido Iridium P-C-P Pincer Complex

M. GUPTA, C. HAGEN, W. C. KASKA, R. E. CRAMER and C. M. JENSEN, *J. Am. Chem. Soc.*, 1997, **119**, (4), 840–841

The Ir P-C-P pincer complex  $\text{IrH}_2\{\text{C}_6\text{H}_5\text{-2,6-(CH}_2\text{-PBu}_2\text{)}_2\}$  is reported as a highly active, completely catalytic homogeneous system for the transfer dehydrogenation of cycloalkanes to arenes. The unique reactivity is due to the P-C-P ligand, which renders the metal centre reactive with saturated hydrocarbons, but restricts its access to the ligand P-C bonds.

### Ruthenium-Catalyzed Dimerization of Terminal Alkynes Initiated by a Neutral Vinylidene Complex

C. SLUGOVČ, K. MEREITER, E. ZOBETZ, R. SCHMID and K. KIRCHNER, *Organometallics*, 1996, **15**, (25), 5275–5277

The complexes  $\text{RuTp}(\text{PPh}_3)_2\text{Cl}$ ,  $\text{RuTp}(\text{PPh}_3)(\text{py})\text{Cl}$  and  $\text{RuTp}(\text{PPh}_3)_2\text{H}$  (Tp = trispyrazolylborate, py = pyridine) catalyse the dimerisation of  $\text{HC}\equiv\text{CR}$  (R = Ph, SiMe<sub>3</sub>, *n*-Bu and *t*-Bu) to give 1,4- and 2,4-disubstituted butenyne. The conversion depends upon the choice of solvent, and both the conversion and selectivity depend strongly upon the nature of the alkyne substituent.

## FUEL CELLS

### CO-Stabilized Supported Pt Catalysts for Fuel Cells: Radiolytic Synthesis

B. LE GRATIET, H. REMITA, G. PICQ and M. O. DELCOURT, *J. Catal.*, 1996, **164**, (1), 36–43

$\text{K}_2\text{PtCl}_4$  was radiolytically reduced in a CO-saturated  $\text{H}_2\text{O}/2$ -propanol mixed solvent, either into molecular carbonyl clusters of the  $[\text{Pt}_n(\text{CO})_n]^{2-}$  series or into colloidal metal particles by changing the CO:Pt ratio. The colloidal Pt and also the molecular clusters can be easily impregnated on C black, giving catalysts which are efficient for MeOH or  $\text{H}_2$  electrooxidation and  $\text{O}_2$  electroreduction. These particles, 2–3 nm in size, are independent of the catalyst loading and support surface area, even for high loadings.

### Analysis of the Electrochemical Characteristics of a Direct Methanol Fuel Cell Based on a Pt-Ru/C Anode Catalyst

A. S. ARICÒ, P. CRETÌ, H. KIM, R. MANTEGNA, N. GIORDANO and V. ANTONUCCI, *J. Electrochem. Soc.*, 1996, **143**, (12), 3950–3959

A vapour-feed DMFC based on a Nafion 117<sup>®</sup> solid polymer electrolyte was studied using Pt-Ru/C (1) and Pt/C (2) catalysts for MeOH oxidation and  $\text{O}_2$  reduction, respectively. Crystalline f.c.c. phases were found in the Pt and Pt-Ru catalysts, but the alloy composition in the latter differed from the nominal composition. An increase in the average particle size and particle agglomeration was observed in (1) compared to (2). The electrochemical performance of a DMFC was thus enhanced and output power density of ~150  $\text{mWcm}^{-2}$  was achieved with low Pt loadings.

### Electrooxidation of CO and $\text{CO}/\text{H}_2$ Mixtures on a Pt-Sn Catalyst Prepared by an Implantation Method

N. M. MARKOVIĆ, A. WIDELÓV, P. N. ROSS, O. R. MONTEIRO and I. G. BROWN, *Catal. Lett.*, 1997, **43**, (3, 4), 161–166

A novel ion implantation technique is used to create a non-equilibrium Pt-Sn(IMP) (IMP is implanted) near surface alloy with ~8.6 at.% Sn. The kinetics of the electrooxidation of CO and 2%  $\text{CO}/\text{H}_2$  mixtures on Pt-Sn(IMP) are nearly identical to those of  $\text{Pt}_3\text{Sn}(110)$ . This method may lead to a new Pt-Sn alloy fuel cell catalyst with a unique surface composition of Sn.

## Five Percent Platinum-Tungsten Oxide-Based Electrocatalysts for Phosphoric Acid Fuel Cell Cathodes

O. SAVADOGO and P. BECK, *J. Electrochem. Soc.*, 1996, 143, (12), 3842-3846

A Pt-W oxide-based electrocatalyst was produced by an inexpensive chemical route for use as an O<sub>2</sub> cathode in 99% H<sub>3</sub>PO<sub>4</sub> at 180°C. The electrocatalytic properties for the O<sub>2</sub> reduction reaction (ORR), such as exchange current density and mass activity, of a 5% Pt-40% WO<sub>3</sub>-based electrode (1) were twice as high as those of 10% Pt, due to an increase in its electrochemically active surface. The performance of (1) for ORR was compared to that for a 2% Pt-1% H<sub>2</sub>WO<sub>4</sub>-based electrode, and found to be lower.

## CORROSION PROTECTION

### Hot Corrosion Behavior of Pt-Al Coating in Molten Sulphate or Mixed Salts

Y. PANG, H. GUAN, X. SUN and X. JIANG, *Corros. Sci. Prot. Technol.*, 1997, 9, (1), 34-37

The hot corrosion behaviour of a Pt-modified aluminate coating on superalloys in the presence of molten Na<sub>2</sub>SO<sub>4</sub>, or Na<sub>2</sub>SO<sub>4</sub> + NaCl, salts was studied in air at 900°C. The coating displayed good hot corrosion resistance in molten sulfate, forming only a protective Al<sub>2</sub>O<sub>3</sub> layer on the surface. The addition of NaCl into the Na<sub>2</sub>SO<sub>4</sub> strongly decreased this resistance and the Pt-Al coating suffered from internal oxidation and sulfidation, while its inner NiAl phase showed even greater corrosion.

### Corrosion Resistance of Titanium-Platinum Alloy Prepared by Spark Plasma Sintering

J. ONAGAWA, T. GOTO, O. ISE, N. ISHII, T. HORIKAWA and K. SAWADA, *Mater. Trans. JIM*, 1996, 37, (11), 1699-1703

The corrosion resistance and microstructure of Ti-Pt alloys, prepared from Ti and Pt powders using spark plasma sintering, were studied by SEM and XRD. The Pt phases were dispersed throughout the Ti matrix, and some Ti-Pt intermetallic compounds were formed around the Pt phases. The corrosion resistance of Ti was improved by the addition of traces of Pt and by annealing, which created a eutectic state between the Pt and TiPt phases.

## CHEMICAL TECHNOLOGY

### Purification of Rhodium-Filled Carbon Nanotubes Using Reversed Micelles

J. COOK, J. SLOAN, R. J. R. HEESOM, J. HAMMER and M. L. H. GREEN, *Chem. Commun.*, 1996, (23), 2673-2674

A non-invasive, external washing method for RhCl<sub>3</sub> filled nanotubes used a reversed micelle medium formed from dodecylammonium propionate (dap)-solubilised water in benzene. Treatment with H<sub>2</sub> at 500°C for 5h gave nanotubes filled with discrete crystals of Rh metal, but with no crystals on the exterior of the structures. These materials may find uses as nanowires, composites and catalysts.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Thermal Reliability and Characterization of InGaP Schottky Contact with Ti/Pt/Au Metals

C.-T. LEE, H.-P. SHIAO, N.-T. YEH, C.-D. TSAI, Y.-T. LYU and Y.-K. TU, *Solid-State Electron.*, 1997, 41, (1), 1-5

The characteristics of Ti/Pt/Au Schottky contacts on wide bandgap InGaP semiconductors, with surface pretreatment before Schottky contact deposition, and the effect of post heat treatment on Schottky diodes (1) are presented. Predeposition surface etching by dilute HCl, dilute NH<sub>4</sub>OH, or buffer oxide etchant greatly improved the performance of (1). After annealing (1) at 500°C, a drastic degradation of the barrier height and the ideality factor occurred. This may be due to the interdiffusion and penetration of metals into the semiconductor.

### Au/Ge/Pd Ohmic Contacts to n-GaAs with the Mo/Ti Diffusion Barrier

C.-Y. CHAI, J.-A. HUANG, Y.-L. LAI, J.-W. WU, C.-Y. CHANG, Y.-J. CHAN and H.-C. CHENG, *J. Electron. Mater.*, 1996, 25, (12), 1818-1822

Three different barrier structures, Au/Ge/Pd/GaAs, Au/Ti/Ge/Pd/GaAs and Au/Mo/Ti/Ge/Pd/GaAs were studied to determine the effects of the As-outdiffusion and Au-indiffusion on their performance. The smoothest surface and the lowest specific contact resistivity were found on Au/Mo/Ti/Ge/Pd/n-GaAs samples, at the widest annealing temperature range. Mo/Ti was an efficient diffusion barrier, retarding Au-indiffusion and As-outdiffusion against thermal annealing.

### The Effects of Processing Conditions on the Resistivity and Microstructure of Ruthenate-Based Thick Film Resistors

F. JOHNSON, G. M. CROSBIE and W. T. DONLON, *J. Mater. Sci., Mater. Electron.*, 1997, 8, (1), 29-37

Resistances were measured *in situ* during firing of blended resistors having a nominal sheet resistivity of 56 kΩ/□ and TCR < ± 100 ppm K<sup>-1</sup>. XRD showed Pb ruthenate, Al<sub>2</sub>O<sub>3</sub>, and Zr silicate in the resistors with the ruthenate lattice parameters increasing with increasing firing temperature and time. Resistance changes are attributed to increased separation of ruthenate particles by coarsening.

## MEDICAL USES

### Kinetics of Nitric Oxide Scavenging by Ruthenium(III) Polyaminocarboxylates: Novel Therapeutic Agents for Septic Shock

N. A. DAVIES, M. T. WILSON, E. SLADE, S. P. FRICKER, B. A. MURRER, N. A. POWELL and G. R. HENDERSON, *Chem. Commun.*, 1997, (1), 47-48

Two Ru(III) polyaminocarboxylates, K[Ru(Hedta)Cl], JM1226, and [Ru(Hedta)(H<sub>2</sub>O)], JM6245, have been shown to rapidly bind NO (rate constant > 10<sup>7</sup> M<sup>-1</sup>s<sup>-1</sup>) tightly (binding constant = 10<sup>8</sup> M<sup>-1</sup>) at physiological pH to form a stable 1:1 Ru(II) mononitrosyl. They have potential as NO scavengers in NO mediated diseases.