

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

CO Chemisorption on Differently Prepared Cu₃Pt(111) Alloy Surfaces

A. HOLZWARTH, J. LOBODA-CACKOVIC, J. H. BLOCK and K. CHRISTMANN, *Z. Phys. Chem. (München)*, 1996, **196**, (1), 55–72

The interaction of CO with single-crystal Cu₃Pt(111) alloy surfaces was studied at 100–900 K. The surface composition and long-range order of Cu₃Pt(111) faces depended strongly on sputtering and annealing conditions; superstructure $p(2 \times 2)$ and phase $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ were detected. The CO binding energy on Pt sites is reduced even at low Cu levels, possibly by electronic (ligand) effects; Cu sites are less affected by Pt.

Thermal Stability and Hydrogen Absorption Characteristics of Palladium-Yttrium Nanoalloys

K. J. BRYDEN and J. Y. YING, *Acta Mater.*, 1996, **44**, (9), 3847–3854

Nanostructured Pd alloys containing 10, 20 and 30 at.% Y were produced by high-energy ball-milling to determine thermal stabilities and hydriding behaviours. A nanoalloy, stable against grain growth to > 400°C, formed on adding 10 at.% Y to Pd. With 20 and 30 at.% Y, a supersaturated solution of Y in Pd and in the Pd₃Y intermetallic phase formed, respectively. Both were stable against grain growth to > 400°C and had phase segregation during heat treatment. Doping Pd with Y also suppressed the $\alpha \rightarrow \beta$ phase transition.

Superconductivity in CuRh₂(S_{1-x}Te_x)₄

N. KIJIMA, H. YASHIRO and S. NAGATA, *J. Phys. Chem. Solids*, 1996, **57**, (11), 1635–1639

Transport and magnetic properties of cubic spinel solid solution system CuRh₂(S_{1-x}Te_x)₄ ($0 \leq x \leq 0.1$), prepared by a solid-state reaction technique, were investigated. Lattice constant, a , increased rapidly for $x \leq 0.02$ with increased Te levels, but was insensitive to x for $0.02 \leq x \leq 0.1$. The superconducting transition temperature, T_c , decreased abruptly for $x \leq 0.02$, then linearly with x , which may be due to decreases in the density of state at the Fermi level on Te substitution.

Preparation and Thermoelectric Properties of Ir_xCo_{1-x}Sb₂ Alloys

T. CAILLAT, *J. Phys. Chem. Solids*, 1996, **57**, (9), 1351–1358

Arsenopyrite compounds CoSb₂ and IrSb₂ and Ir_xCo_{1-x}Sb₂ alloys (1) were prepared and characterised. Polycrystalline samples of IrSb₂ and (1) were prepared by hot-pressing prereacted powders. A range of solid solutions existed for (1) for $0.1 \leq x \leq 0.8$. All materials are semiconductors of p -type conductivity. A band gap of ~ 0.98 eV was calculated for IrSb₂.

New Results about the Osmium-Zirconium System

K. MAHDOUK, B. SUNDMAN and J.-C. GACHON, *J. Alloys Compd.*, 1996, **241**, 199–209

A thermodynamic study of the binary system Os–Zr was carried out and a first complete version of the phase diagram proposed. Direct reaction calorimetry at high temperature gave enthalpies of formation in J(at. mol)⁻¹ of Os_{0.50}Zr_{0.50} ($\Delta_f H = -40,500 \pm 1400$), Os_{0.33}Zr_{0.67} ($\Delta_f H = -20,500 \pm 2500$) and Os_{0.246}Zr_{0.754} ($\Delta_f H = -28,800 \pm 1200$). Two intermetallic compounds, OsZr₂ and Os₁₇Zr₅₄, were discovered.

Hall-Effect Sign Reversal in CaRuO₃ and SrRuO₃ Thin Films

S. C. GAUSEPOHL, M. LEE, R. A. RAO and C. B. EOM, *Phys. Rev. B*, 1996, **54**, (13), 8996–8999

Epitaxial thin films of metallic oxides CaRuO₃ and SrRuO₃ showed a Hall effect sign change from negative to positive as temperature was increased through ~ 50 K. This, together with the low- and high-temperature magnitudes of the Hall coefficients, indicates that CaRuO₃ and SrRuO₃ are highly compensated metals. The sign change suggests that large regions of the Fermi surfaces have nearly zero band curvature.

Hall Effect in the Two-Dimensional Metal Sr₂RuO₄

A. P. MACKENZIE, N. E. HUSSEY, A. J. DIVER, S. R. JULIAN, Y. MAENO, S. NISHIZAKI and T. FUJITA, *Phys. Rev. B*, 1996, **54**, (10), 7425–7429

The Hall effect was studied in Sr₂RuO₄, the first layered perovskite superconductor without Cu ($T_c \cong 1$ K). The Hall coefficient (R_H) at 20 mK–300 K has an unusual dependence on the applied magnetic field and a strong temperature dependence < 25 K, but below 1 K it saturates at $-1.15 \times 10^{-10} \text{ m}^3 \text{ C}^{-1}$. The strong temperature dependence of R_H at higher temperatures may be due to small temperature dependent changes in the \mathbf{k} dependence of the mean free path, l .

CHEMICAL COMPOUNDS

Synthesis and Isolation of Cuboctahedral and Icosahedral Platinum Nanoparticles. Ligand-Dependent Structures

A. RODRIGUEZ, C. AMIENS, B. CHAUDRET, M.-J. CASANOVE, P. LECANTE and J. S. BRADLEY, *Chem. Mater.*, 1996, **8**, (8), 1978–1986

The synthesis of small (12–17 Å) Pt particles with a narrow size distribution stabilised by CO alone, CO and THF, or CO, THF and triphenylphosphine, are reported. They contain only zerovalent Pt and their structures are f.c.c. or icosahedral, depending on the nature of the ligands. These colloids are stable, and can be isolated and handled like molecular species.

Structures and Spectroscopic Properties of the Pt(dpp)X₂ (dpp = 2,3-bis(2-pyridyl)pyrazine) Building Blocks and the Photophysical Properties of Heterometallic M-dpp-Pt Supermolecules (M = Ru, Re, Pt)

Y.-Y. NG, C.-M. CHE and S.-M. PENG, *New J. Chem.*, 1996, 20, (7/8), 781–789

The complexes Pt(dpp)X₂ (where dpp = 2,3-bis(2-pyridyl)pyrazine; X = Cl, Ph, C≡CPh and CN) have been synthesised. All display luminescence in the solid state while the last two are also emissive in solution at room temperature. The emissive properties of the heterometallic supramolecular complexes [Ph₂Pt(dpp)-Ru(5,5'-Me₂bpy)₂](ClO₄)₂ (5,5'-Me₂bpy = 5,5'-dimethyl-2,2'-bipyridine), (PhC≡C)₂Pt(dpp)Re(CO)₂Cl and Ph₂Pt(dpp)PtCl₂ have also been studied.

Supramolecular Self-Assembly of Macrocycles, Catenanes, and Cages through Coordination of Pyridine-Based Ligands to Transition Metals

M. FUJITA and K. OGURA, *Bull. Chem. Soc. Jpn.*, 1996, 69, (6), 1471–1482

A review is given of transition metal-mediated supramolecular self-assembly with focus on the generation of macrocycles, hollow cages and catenanes from the *cis*-protected Pd(II) complex, (en)Pd(NO₂)₂, with pyridine-based bridging ligands. This system provides 90° angles from which the structures can be assembled. The bonding of linear 4,4'-bipyridine to the (en)Pd(NO₂)₂ results in a macrocyclic square supramolecule. This concept is extended to three-dimensional cage-like supramolecules that can encapsulate organic molecules.

Organometallic Hydrides as Reactants in Fullerene Chemistry. Interaction of the Fullerenes C₆₀ and C₇₀ with HM(CO)(PPh₃)₃ (M = Rh and Ir) and HIr(C₆H₁₂)(PPh₃)₂

A. V. USATOV, K. N. KUDIN, E. V. VORONTOV, L. E. VINOGRADOVA and Y. N. NOVIKOV, *J. Organomet. Chem.*, 1996, 522, (1), 147–153

The fullerenes C₆₀ and C₇₀ reacted with the Rh and Ir hydride complexes HM(CO)(PPh₃)₃ (M = Rh and Ir) and HIr(COD)(PPh₃)₂ with high regio- and stereo-selectivity, forming only the η²-derivatives (η²-C_n)MH(CO)(PPh₃)₃, where n = 60 or 70 and (η²-C₆₀)IrH(C₆H₁₂)(PPh₃)₂, respectively. The metal atom is co-ordinated with the C₆₀ and C₇₀ molecules at the 1,2 and 1,9 bonds, respectively.

Cationic Iridium(III) Carbonyl Complexes: [Ir(CO)₆]³⁺ and [Ir(CO)₅Cl]²⁺

C. BACH, H. WILLNER, C. WANG, S. J. RETTIG, J. TROTTER and F. AUBKE, *Angew. Chem., Int. Ed. Engl.*, 1996, 35, (17), 1974–1976

The first homoleptic carbonyl cation of a tripositive metal, [Ir(CO)₆]³⁺, is reported as the thermally stable [Sb₂F₁₁]⁻ salt. This allows a comparison of the spectroscopic properties in the 5d series of isoelectronic hexacarbonyl species ranging from [Hf(CO)₆]²⁺ to [Ir(CO)₆]³⁺. The structure of [Ir(CO)₅Cl]²⁺ is given.

New Water-Soluble Ruthenium(II) and Osmium(II) Hydroxo Carbonyl Complexes

E. CARIATI, E. LUCENTI, M. PIZZOTTI, D. ROBERTO and R. UGO, *Organometallics*, 1996, 15, (20), 4122–4124
H₂O-soluble and air-stable species [Ru(CO)₂Cl(OH)]_n, [Ru(CO)₂(OH)₂]_n, [Os(CO)₂Cl(OH)]₂ and [Os(CO)₂(OH)₂]_x (x = 2 or n) were prepared from the reaction of [M(CO)₂Cl]₂ (M = Ru, Os) (1) with aqueous NaOH. These complexes could be the active species involved in the high-yield SiO₂-mediated synthesis of various Os and Ru carbonyl clusters starting from (1) in the presence of alkali-metal carbonates. A simple method to define the number of carbonyl ligands is presented.

Structure and Conductivity of an Electrocrystallized Ruthenium[1,8]-Binaphthyridine Complex

E. PÉREZ-CORDERO, N. BRADY, L. ECHEGOYEN, R. THUMMEL, C.-Y. HUNG and S. G. BOTT, *Chem. Eur. J.*, 1996, 2, (7), 781–788

The crystal structure of [Ru-(binap-2)](PF₆)₂ (1) (binap-2 = 3,3'-dimethylene-2,2'-bi[1,8]naphthyridine) and its one-electron reduction product [Ru-(binap-2)](PF₆) (2) are reported. Crystals of (2) behave as semiconductors, with a band gap of 0.53 eV, while those of (1) are insulating. In (2) the extra electron appears over two binap-2 ligands while the third ligand, orthogonal to the other two, appears to contain no appreciable electron density. The crystal lattice packing shows many intermolecular stacking interactions. Electron density may be shifted between ligand systems by photoexcitation, changing the conduction properties along the orthogonal axes.

Synthesis, Molecular Structure and Reactions of Stable Square-Planar 16-Electron Ruthenium(0) Complexes: *trans*-[RuCl(NO)(PR₃)₂]

R. FLÜGEL, B. WINDMÜLLER, O. GEVERT and H. WERNER, *Chem. Ber.*, 1996, 129, (9), 1007–1013

The reduction of RuCl₂(NO)(PPh₃)₂ with Zn/Cu generates RuCl(NO)(PPh₃)₂. Ligand exchange with PR₃ (R₃ = *i*Pr₃, *i*Pr₂Ph) gives the stable 16-electron Ru(0) complexes *trans*-[RuCl(NO)(PR₃)₂]. These electronically and co-ordinatively unsaturated compounds oxidatively add Brønsted acids, such as HCl, as well as reacting with Lewis bases, such as CO, TCNE, CH₂ and O₂, to form 1:1 adducts. The O₂ complexes also react with SO₂ to give sulfato-Ru (II) derivatives.

Synthesis and Property of Planar-Chiral Cyclopentadienyl-Ruthenium Complexes

N. KOMATSUZAKI, M. UNO, H. KIKUCHI and S. TAKAHASHI, *Chem. Lett. Jpn.*, 1996, (8), 677–678

The first enantiomerically pure planar-chiral cyclopentadienyl-Ru complexes, [CpⁿRu(benzene)]PF₆, (CpⁿH = unsymmetrically trisubstituted cyclopentadiene) are reported. Photolysis in the presence of acetonitrile leads to [CpⁿRu(CH₃CN)₃]PF₆ which can be transformed into the planar-chiral complex [CpⁿRu(arene)]PF₆ via ligand exchange.

Synthesis and Crystal Structures of Thiolate-Bridged Diruthenium Complexes Containing Two Olefinic Ligands

J.-P. QÜ, H. MATSUZAKA, Y. ISHII and M. HIDAI, *Chem. Lett. Jpn.*, 1996, (9), 767-768

A series of thiolate-bridged dinuclear Ru complexes containing two electron-deficient olefinic ligands [$\text{Cp}^*\text{Ru}(\mu\text{-SR})_2(\eta^2\text{-C}_2\text{H}_3\text{R}')_2\text{RuCp}^*$] ($\text{R} = \text{Pr}^i, \text{Et}, 2,6\text{-C}_6\text{H}_3\text{Me}_2$ or $2,4,6\text{-C}_6\text{H}_2\text{Me}_3$; $\text{R}' = \text{CN}, \text{COOMe}$ or CHO) have been synthesised from the reactions of Ru(II)-Ru(II), Ru(II)-Ru(III) and/or Ru(III)-Ru(III) precursors with acrylonitrile.

ELECTROCHEMISTRY

Surface Area Loss of Platinum Alloy Supported on Carbon in Concentrated Phosphoric Acid at Low Potentials

T. MAOKA, M. UENO, T. KUWABARA and H. NISHIKAWA, *Denki Kagaku*, 1996, 64, (6), 431-435

The electrochemically active surface area of a Pt alloy supported on C in hot concentrated H_3PO_4 , held at a potential below the double layer region of Pt, was measured by cyclic voltammetry. The surface area initially decreased considerably, then recovered again when the electrode was held at higher potentials. This was also observed when Pt foil was used as a test electrode. However, the crystallite diameter did not change much after immersion, probably due to the blocking of active surface sites with impurities in H_3PO_4 at low potentials.

On the Adsorption and Reduction of NO_3^- Ions at Au and Pt Electrodes Studied by *in situ* FTIR Spectroscopy

M. C. P. M. DA CUNHA, M. WEBER and F. C. NART, *J. Electroanal. Chem.*, 1996, 414, (2), 163-170

The adsorption of nitrate ions on Au and Pt electrodes in acidic solution is studied by *in situ* FTIRS. Pt electrodes are found to be more active catalytically to nitrate reduction than Au electrodes. At the Pt electrodes, NO_3^- ions are readily reduced at potentials below 0.8 V, generating adsorbed NO at low surface coverages.

Electrocatalytic Hydrogenation of Acetylenes on Palladium Incorporating Poly[*N*-(5-Hydroxypentyl)Pyrrole] Film-Coated Electrode

N. TAKANO, Y. KAWAKAMI and N. TAKENO, *Chem. Lett. Jpn.*, 1996, (8), 589-590

Catalytic polymer film electrodes were made from poly[*N*-(5-hydroxypentyl)pyrrole] electrochemically coated on either grassy C plates or fibres. Onto these were deposited Pd metal microparticles. These electrodes were used for the electrochemical hydrogenation of acetylenes (phenylacetylene, diphenylacetylene and dimethyl acetylenedicarboxylate) in an organic solvent-HCl buffer, which resulted in the formation of the corresponding ethanes in good yields (93-100%) and with high current efficiencies (87-99%).

Electroreductive Cleavage of Propargylic Acetates Through Polarity Inversion of *in situ* Generated Allenyl Palladium(II) Complexes and, in Part, Unusual Chemical Reduction Induced by Phosphine Ligand

H. TANAKA, H. TAKEUCHI, Q. REN and S. TORII, *Electroanalysis*, 1996, 8, (8-9), 769-772

The electroreduction of propargyl acetates in the presence of a catalytic amount of $\text{PdCl}_2(\text{PPh}_3)_2/\text{PPh}_3$ in DMF containing Et_4NOT s at ambient temperature under a constant current density of 10 mA cm^{-2} yielded the corresponding allenes in 43-84% yield. The reductive cleavage of propargylic acetates into the allenes was completed with less than the theoretical amount of electricity, 2F mol^{-1} , which suggests the *in situ* generation of the allenyl Pd(II) complex.

Effect of Coating Thickness and Surface Treatment of Titanium on the Properties of $\text{IrO}_2\text{-Ta}_2\text{O}_5$ Anodes

J. KRÝSA, L. KULE, R. MRÁZ and I. ROUŠAR, *J. Appl. Electrochem.*, 1996, 26, (10), 999-1005

The effects of coating thickness and surface treatment of the Ti base metal on the surface morphology of Ti/ $\text{IrO}_2\text{-Ta}_2\text{O}_5$ anodes were studied. The service life of the coatings was proportional to Ir contents, for 0.45-1.2 mg Ir cm^{-2} . A macrorough surface formed during etching of Ti in 5% HF at 25°C, but during etching in HCl at 30, 50 and 80°C a microrough surface with visible pitting formed. The morphology of the $\text{IrO}_2\text{-Ta}_2\text{O}_5$ active layer with 0.32-0.39 mg Ir cm^{-2} depended on the pretreatment of the Ti base. The service life of the $\text{IrO}_2\text{-Ta}_2\text{O}_5$ layer was 1500 ± 400 h in 0.5 M H_2SO_4 , at 25°C and current density of 2 A cm^{-2} .

PHOTOCONVERSION

Preparation of Langmuir-Blodgett Film of a Platinized Viologen-Linked Porphyrin and Photoinduced Hydrogen Evolution

H. HOSONO, T. TANI and I. UEMURA, *Chem. Commun.*, 1996, (16), 1893-1894

Langmuir-Blodgett films were platinized by dipping into an Ar purged aqueous solution of $\text{H}_2\text{N}_2\text{edta}$ and H_2PtCl_6 , then irradiating for 72 h with visible light. The Pt particles were fixed in the LB film close to the viologen. When used for photoinduced H_2 evolution, the fixed Pt catalyst was stable and the H_2 evolution rate was constant. After 240 h irradiation the turnover number of viologen-linked porphyrin reached 265.

Visible Light Emission from the Porous Alloyed Pt/Si Contacts

T. ICHINOHE, S. NOZAKI and H. MORISAKI, *Thin Solid Films*, 1996, 281-282, (1-2), 610-612

Chemical composition and photoluminescence studies were performed on porous anodised alloyed Pt/Si contacts, with composition depending strongly on alloying temperature. When exposed to the 488 nm line of an Ar ion laser light the Pt/Si contacts emitted red light of wavelength 600-800 nm.

Minority Carrier Controlled PEC Solar Cells, Using *n*-Si Electrodes Modified with LB Layers of Ultrafine Pt Particles

S. YAE, M. FUJITANI, I. NAKANISHI, M. UETSUJI, R. TSUDA and Y. NAKATO, *Solar Energy Mater. Solar Cells*, 1996, **43**, (3), 311–318

The effects of the Pt particle density and the post-heat treatment temperature on the open-circuit photovoltages (V_{OC} s) of photoelectrochemical (PEC) solar cells having *n*-Si electrodes modified with ultrafine Pt particles were studied. The Pt particle density on the *n*-Si was controlled by Langmuir-Blodgett layers of Pt-colloid particles stabilised by polyvinylpyrrolidone. When the Pt-modified *n*-Si electrodes were heat-treated at 150°C or not, the V_{OC} was 0.61–0.63 V, independent of Pt density, indicating that minority carrier controlled solar cells were obtained.

Hydrogen Evolution on Platinum-Coated *p*-Silicon Photocathodes

C. U. MAIER, M. SPECHT and G. BILGER, *Int. J. Hydrogen Energy*, 1996, **21**, (10), 859–864

The effect of various surface morphologies of Pt-coated *p*-Si electrodes on the photoelectrochemical formation of H_2 was investigated. The electrocatalytic activity and the stability of monocrystalline Pt-coated *p*-type Si electrodes was improved using different Pt films prepared by various deposition processes. High photovoltages, from high Schottky barriers necessary for efficient H_2 evolution, were observed for heterogeneous Pt deposition on *p*-Si with Pt island structures.

Diastereoselective Intramolecular C-H Bond Activation by Optically Active Tris(pyrazolyl)hydroborate Complexes of Rhodium

M. C. KEYES, V. G. YOUNG and W. B. TOLMAN, *Organometallics*, 1996, **15**, (20), 4133–4140

Photolysis of the optically active complexes $Tp^*Rh(CO)_2$, where Tp^* are C_3 -symmetric ligands T^{Menth} or T^{Menth} , prepared by metathesis of the respective $TiTp^*$ with $[Rh(CO)_2Cl]_2$ in CH_2Cl_2 , yielded chiral alkyl-hydride complexes resulting from intramolecular cyclometallations that proceeded with high overall diastereoselectivity and complete enantiocontrol at the metal.

ELECTRODEPOSITION AND SURFACE COATINGS

Organometallic Chemical Vapour Deposition of Palladium under Very Mild Conditions of Temperature in the Presence of a Low Reactive Gas Partial Pressure

J. -C. HIERO, C. SATTO, R. FEURER and P. KALCK, *Chem. Mater.*, 1996, **8**, (10), 2481–2485

Pd thin-film deposition was carried out from the known precursors $Pd(\eta^1-C_5H_5)(Cp)$ ($Cp = \eta^1-C_5H_5$) and $Pd(\eta^1-C_5H_5)(hfa)$ ($hfa = CF_3COCHCOCF_3$). The addition of 1% H_2 to the He carrier gas, introduced in the vapour phase, allowed the Pd to be deposited on the substrate at very low temperatures (30–60°C) and with high purity levels.

Characteristics of Conductive SrRuO₃ Thin Films with Different Microstructures

Q. X. JIA, F. CHU, C. D. ADAMS, X. D. WU, M. HAWLEY, J. H. CHO, A. T. FINDIKOGLU, S. R. FOLTYN, J. L. SMITH and T. E. MITCHELL, *J. Mater. Res.*, 1996, **11**, (9), 2263–2268

Conductive SrRuO₃ thin films were epitaxially grown on (100) LaAlO₃ substrates by pulsed laser deposition at 650–825°C. The degree of crystallinity of the films improved with increasing deposition temperature and the resistivity of the films was found to be strongly dependent on this crystallinity. A residual resistivity ratio of > 8 was obtained for the SrRuO₃ thin films deposited under optimised conditions.

APPARATUS AND TECHNIQUE

Fabrication of a Platinum Dual-Disk Microelectrode and Investigation of Its Properties

C. ZHANG and X. ZHOU, *J. Electroanal. Chem.*, 1996, **415**, (1–2), 65–70

Pt dual-disk microelectrodes with interelectrode gaps of 5–40 μm were constructed by fixing two 60 μm diameter Pt wires onto a glass slide with epoxy resin. The collection efficiency for a dual-disk microelectrode with a gap of 5 μm is 44.4%. Both increased temperature and stirring resulted in an increase of the generator current. The collection efficiency is not as high as for dual-cylinder C-fibre microelectrodes but they are easier to produce and their surfaces can be renewed frequently. They are good generation-collection devices.

Selective Construction of Electrical Connections Using an Organic Charge-Transfer Salt

C. GURTNER and M. J. SAILOR, *Adv. Mater.*, 1996, **8**, (11), 897–899

A method for constructing electrical connections between two Pt wires by AC electrocrystallisation of tetrathiafulvalenium bromide $TTFBr_x$ ($x = 0.74–0.79$) from a non-aqueous solution is described. This procedure results in 3-D interconnecting structures without the aid of a photolithographic or morphologic template. The material can be readily crystallised or dissolved, thus allowing construction of connections and the removal of mistakes. The technique should be applicable to nanofabrication.

Electrocatalysis and Amperometric Detection of Aliphatic Aldehydes at Platinum-Palladium Alloy Coated Glassy Carbon Electrode

J. WANG, P. V. A. PAMIDI and G. CEPRIA, *Anal. Chim. Acta*, 1996, **330**, (2–3), 151–158

Aliphatic aldehydes undergo electrocatalytic oxidation at a Pt-Pd alloy coated glassy C electrode. Modifying the alloy produces highly sensitive and stable, constant-potential (+0.35 V) amperometric detection of simple aldehydes. Formaldehyde, acetaldehyde and propionaldehyde were detected in flow-injection analysis at levels as low as 0.9, 6.4 and 6.5 ng (30, 160 and 120 pmol), respectively.

Graphite-Furnace Atomic Absorption Spectrometry of Organomercury and Organoselenium in Extracts of Biological Samples with an Organopalladium Matrix Modifier

H. LI, H. NAGASAWA and K. MATSUMOTO, *Anal. Sci.*, 1996, 12, (2), 215–218

The sensitivity of organomercury in organic solutions is improved by applying 15 μl of an EtOH solution of $\text{Pd}(\text{acac})_2$ (500 $\mu\text{g Pd ml}^{-1}$, acac = acetylacetonate) to a graphite furnace to form a Pd coating. This gives a detection limit for organomercury of 0.25 ng. Similarly, using $\text{PdCl}_2(\text{PhCN})_2$ (1000 $\mu\text{g Pd ml}^{-1}$), Se can be determined to a limit of 0.12 ng. This method can be successfully used for environmental samples.

Preparation of Pd Thin Film Photo-Cathodes Using Ion-Beam Sputtering

T. NOSAKA, M. YOSHITAKE, A. OKAMOTO, Y. SUZUKI, S. OGAWA and H. MIMA, *Thin Solid Films*, 1996, 281–282, (1–2), 393–396

A new type of vacuum gauge using a Pd thin film photocathode was prepared on a quartz substrate by ion-beam sputtering. The photoelectron current emitted from the Pd thin film increased with decreasing film thickness. A maximum current of 240 nA was obtained from a 4 nm film. An ionisation gauge using a Pd photocathode of 7 nm thickness had a linear response over the range 10^{-2} – 10 Pa in Ar gas. Sputtering conditions affected the photoelectric emission from the Pd surface on UV irradiation.

Fabrication of a Thin Palladium Membrane Supported in a Porous Ceramic Substrate by Chemical Vapor Deposition

G. XOMERITAKIS and Y. S. LIN, *J. Membrane Sci.*, 1996, 120, (2), 261–272

Thin and fairly gas-tight Pd membranes were prepared inside a supported $\gamma\text{-Al}_2\text{O}_3$ membrane by counter-diffusion chemical vapour deposition using PdCl_2 vapour and H_2 as Pd precursors. A disk-shaped, two-layer porous ceramic membrane with a top layer of a fine-pore $\gamma\text{-Al}_2\text{O}_3$ and a coarse-pore $\alpha\text{-Al}_2\text{O}_3$ substrate was used as the Pd membrane support. A 0.5–1 μm thick metallic membrane was deposited in the $\gamma\text{-Al}_2\text{O}_3$ top layer very close to its surface. Pd deposition in the $\gamma\text{-Al}_2\text{O}_3$ layer produced a 10^2 – 10^3 -fold reduction in He permeance in the porous substrate.

HETEROGENEOUS CATALYSIS

Study of Pt-Ce/KL and Pt/CeKL Zeolite Reforming Catalysts

W. LU, F. LI, R. LONG and H. WAN, *Chinese J. Catal.*, 1996, 17, (5), 415–418

A reforming Pt/KL catalyst was modified with Ce by co-impregnation on zeolite KL, forming Pt-Ce/KL, or by ion-exchange into KL, forming Pt/CeKL. The addition of Ce improved the aromatisation activity and selectivity for C_8H_{14} on the Pt-Ce/KL catalyst and its S resistance, however Pt/CeKL had lower activity for C_8H_{14} aromatisation. Pt particles in Pt/CeKL were electron deficient, which decreased the activity.

Preparation of Metallic Palladium Catalysts with Thermally Stable Surface Areas and Activities

S. YADA, T. SASAKI, M. HIYAMIZU and Y. TAKAGI, *Bull. Chem. Soc. Jpn.*, 1996, 69, (8), 2383–2386

Pd metal catalysts were prepared by reacting Pd(II) chloride with Na aluminate (Type A), or NaOH (Type N), at pH 6, 8 or 10. Type A catalysts prepared at pH 10, contaminated with only small amounts of Al (0.14 wt.%) were the most thermally stable and retained large surface areas and high catalytic activities for the hydrogenation of nitrobenzene even after H_2 treatment at $\leq 380^\circ\text{C}$. This was in contrast to Type N catalysts. In the hydrogenation of *p*-cresol to 4-methylcyclohexanol Type A catalyst was ~ 4 times as active as Type N catalyst.

Alloy Formation and Stability in Pd-Cu Bimetallic Catalysts

M. FERNÁNDEZ-GARCÍA, J. A. ANDERSON and G. L. HALLER, *J. Phys. Chem.*, 1996, 100, (40), 16247–16254

The temperature-programmed reduction of three Pd-Cu/KL-zeolite bimetallic catalysts has been studied using X-ray absorption near edge spectroscopy (XANES) and IR spectroscopy with the probe molecule CO. Complete alloying with electronic modification of both components (with respect to their metallic states) is reached for all compositions analysed. The effect of reduction temperature on the nature of the surfaces exposed by the active phases, as well as the sintering process, is primarily governed by the Pd:Cu ratio.

Effective Hydrocracking of 4,6-Dimethyldibenzothiophene Catalyzed by Palladium- and Nickel-Co-Loaded Y-Type Zeolite

K. KANEDA, T. WADA, S. MURATA and M. NOMURA, *Chem. Lett. Jpn.*, 1996, (9), 829

A Pd- and Ni-co-loaded Y-type zeolite catalyst was used in the hydrocracking of DMDBT (DMDBT = 4,6-dimethyldibenzothiophene). The Pd-Ni-H-Y catalyst was prepared by ion-exchange from NH_4 -substituted zeolite with $[\text{Pd}(\text{NH}_3)_4](\text{NO}_3)_2$ followed by $\text{Ni}(\text{NO}_3)_2$ aqueous solution. At 320 – 340°C and under 70 kg cm^{-2} of H_2 pressure, DMDBT was almost completely converted to gases (C_2 – C_4), benzene and cyclohexane derivatives, and H_2S .

Carbonylation Reactions of $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ and $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ in the Solid State

F. PORTA, S. TOLLARI, C. BIANCHI and S. RECCHIA, *Inorg. Chim. Acta*, 1996, 249, (1), 79–83

$\text{Rh}(\text{PPh}_3)_2(\text{CO})\text{Cl}$ and $\text{Ru}(\text{PPh}_3)_2(\text{CO})_2\text{Cl}_2$ (1), complexes were obtained from the solid state carbonylation of $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ (2) and $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ (3), respectively with CO at atmospheric pressure. In the solid state, associative mechanisms mostly cause carbonylation of (2) and the first CO attack on (3) to give (1), an 18-electron species. $\text{Rh}(\text{PPh}_3)_3(\text{CO})\text{Cl}$, a possible intermediate, was stable under N_2 , while Ru intermediate $\text{Ru}(\text{PPh}_3)_3(\text{CO})\text{Cl}_2$ was again attacked by CO.

HOMOGENEOUS CATALYSIS

Platinum(0)-Catalysed Diboration of Alka-1,3-dienes with Bis(pinacolato)diboron

T. ISHIYAMA, M. YAMAMOTO and N. MIYAURA, *Chem. Commun.*, 1996, (17), 2073-2074

The Pt(0) complex Pt(PPh₃)₄ effectively catalyses the addition of bis(pinacolato)diboron to 1,3-dienes. This reaction with isoprene, buta-1,3-diene and 2,3-dimethylbuta-1,3-diene gives the corresponding bis(allyl)boronates in high yields (91–95%) and with high isomeric purities (> 99% (*Z*)-isomer). A similar reaction between isoprene and Pt(dba)₂ gives a product with (*E,E*)-configuration (> 99%) in 94% yield.

Homogeneous Catalysts for Hydrogenation of Unsaturated Hydrocarbons Based on Complexes of Platinum Tetraacetate with Aliphatic Amines

E. G. KLIGER, L. P. SHUIKINA and V. M. FROLOV, *Kinet. Katal.*, 1996, 37, (2), 218-222

Effective Pt catalysts were obtained by the catalytic hydrogenation of unsaturated hydrocarbons based on the products of interaction of Pt(CH₃COO)₄ with aliphatic amines. The kinetic dependence of the hydrogenation reaction was studied. The results showed that a tetraacetate Pt complex with tri-*n*-ion amine has high stability during long reactions with O₂ and H₂O. Catalytic activity occurred on Pt catalysts with hydride branches.

Novel Single-Site Catalysts Containing a Platinum Group Metal and a Macrocyclic Sulfur Ligand for Ethylene Polymerization

S. TIMONEN, T. T. PAKKANEN and T. A. PAKKANEN, *J. Mol. Catal. A: Chem.*, 1996, 111, (1-2), 267-272

The complexes (S₃-ethano-9)RhCl₃ and (S₃-ethano-9)PtCl₄, prepared by the reactions of RhCl₃·3H₂O and PtCl₄ with 1,4,7-trithiacyclononane in EtOH, respectively, catalysed the polymerisation of C₂H₄ in pentane in methylalumoxane at 70°C and under 10 bar C₂H₄ pressure. The macrocyclic S ligand, which acts as protecting group for the metal ion, co-ordinates readily to the Pt centres giving stable complexes.

Excellent Stereocontrol in Intramolecular Buchner Cyclisations and Subsequent Cycloadditions: Stereospecific Construction of Polycyclic Systems

A. R. MAGUIRE, N. R. BUCKLEY, P. O'LEARY and G. FERGUSON, *Chem. Commun.*, 1996, (22), 2595-2596

Highly diastereoselective Rh(II) acetate catalysed intramolecular addition of α -diazo ketones to aromatic rings to form the azulenones (1) was achieved. The Rh(II) acetate catalysed decomposition of α -diazo ketones gave efficient carbenoid addition to the benzene ring. The norcaradiene form of (1) undergoes efficient stereospecific cycloaddition with phenyltriazolinedione, in either a stepwise or a tandem process, leading to pentacyclic systems. The rigid pentacyclic framework produced should lead to carbocyclic intermediates for use in syntheses.

First Palladium-Catalyzed Heck Reactions with Efficient Colloidal Catalyst Systems

M. BELLER, H. FISCHER, K. KÜHLEIN, C.-P. REISINGER and W. A. HERRMANN, *J. Organomet. Chem.*, 1996, 520, (1-2), 257-259

Pd colloids were effective and active catalysts for the olefination of activated aryl bromides in Heck reactions, under optimised conditions. The Pd colloids were prepared in a two step procedure by suspending tetraoctyl NH₄ bromide in THF, then reacting with Na triethyl boronate and PdCl₂. The Pd colloid is stabilised by the excess NH₄ ions. After evaporation the Pd particles were dissolved in dimethylacetamide, to a concentration of 0.05 mmol Pd ml⁻¹. Phosphines strongly retarded the catalyst reaction rate.

Ethanol Oxidation Catalysed by the Giant Clusters of Palladium Pd-561: Acetic Anhydride Formation

M. K. STARCHEVSKII, S. L. GLADII, YA. V. LASTOVYAK, P. I. PASICHNYK, YU. A. PAZDERSKII, M. N. VARGAFTIK and I. I. MOISEEV, *Kinet. Katal.*, 1996, 37, (3), 408-415

The oxidation of EtOH in the presence of giant Pd clusters Pd₅₆₁phen₆₀(OAc)₁₈₀ and Pd₅₆₁phen₆₀(PF₆)₆₀O₆₀, where phen = 1,10-phenanthroline, under mild conditions of 0.1 MPa and 303–323 K proceeded without the presence of free radicals or periodic compounds. Acetaldehyde is the first reaction product, which further converts to acetic anhydride, acetic acid, ethyl acetate and acetal. The reaction mechanism involves intermetallic compounds containing CH₃CHO and CH₃C=O groups, co-ordinated with atomic Pd on the surface of the metallic compound clusters.

Hydroformylation of Olefins in the Presence of Rhodium Carbonyl Catalysts Immobilised on Polymeric Pyrrolidinopyridines

G. V. TEREKHOVA, N. V. KOLESNICHENKO, E. D. ALIEVA, N. A. MARKOVA, N. I. TRUKHMANOVA, E. V. SLIVINSKII and N. A. PLATE, *Izv. Akad. Nauk, Ser. Khim.*, 1996, (7), 1673-1675

The hydroformylation of olefins was studied in the presence of catalytic systems based on RhCl₃ and polymeric pyrrolidinopyridines. High catalytic activity was observed in the hydroformylation of isobutene under conditions in which the activity of conventional homogeneous catalysts is low. These polymeric catalysts are also thermally stable.

Selectivity of Catalytic Systems RhCl₃·Polycation in Hydroformylation of Hex-1-ene under Biphasic Conditions

N. V. KOLESNICHENKO, M. V. SHARIKOVA, T. KH. MURZABEKOVA, N. A. MARKOVA and E. V. SLIVINSKII, *Izv. Akad. Nauk, Ser. Khim.*, 1996, (8), 1968-1971

Various routes to increase the selectivity of H₂O-soluble catalytic systems based on RhCl₃ and polycation in the hydroformylation of hex-1-ene were studied. The introduction of a long-chain alkyl radical into the polycation or the use of a higher fatty acid counterion resulted in an increase in the selectivity of the catalytic system at pH > 7 with respect to *n*-aldehyde to 60%.

Catalytic Polymerization of Phenylacetylene by Cationic Rhodium and Iridium Complexes of Ferrocene-Based Ligands

S.-I. LEE, S.-C. SHIM and T.-J. KIM, *J. Polymer Sci. A: Polymer Chem.*, 1996, **34**, (12), 2377–2386

Complexes of the types [(COD)M(LL)]ClO₄ and [(COD)MCl]₂, where COD = cyclooctadiene, M = Rh, Ir; LL = 1,6-diferrocenyl-2,5-diazahexane (FcNN), etc., were prepared. The Rh complexes were very effective catalysts for phenylacetylene polymerisation, yielding highly stereoregular polyphenylacetylene (*cis-transoidal*-PPA) in high yields under mild conditions. Cationic mononuclear [Rh(FcNN)(COD)]ClO₄ complex showed the best results to yield exclusively the *cis-transoidal*-PPA with the highest molecular weight = 33,340 in 94% yield. The Ir system worked better for trimerisation, giving 1,3,5-triphenylbenzene.

Highly Efficient Enantioselective Synthesis of Optically Active Carboxylic Acids by Ru(OCOCH₃)₂[(S)-H₈-BINAP]

T. UEMURA, X. ZHANG, K. MATSUMURA, N. SAYO, H. KUMOBAYASHI, T. OHTA, K. NOZAKI and H. TAKAYA, *J. Org. Chem.*, 1996, **61**, (16), 5510–5516

The chiral complex Ru(OCOCH₃)₂[(S)-H₈-BINAP] [H₈-BINAP = 2,2'-bis-(diphenylphosphino)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl] is an effective catalyst for the asymmetric hydrogenation of α,β - and β,γ -unsaturated carboxylic acids. The corresponding saturated carboxylic acids are produced in higher *ee* and at faster reaction rates than with the previously reported Ru(OCOCH₃)₂[(R)-BINAP].

The (η^6 -Naphthalene)(η^4 -Cycloocta-1,5-diene)Ruthenium(0) Complex as Precursor for Homogeneous and Heterogeneous Catalysts in the Isomerization of Allyl Ethers and Allyl Acetals to Vinyl Derivatives

P. PERTICI, C. MALANGA, A. GIUNTOLI, G. VITULLI and G. MARTRA, *Gazz. Chim. Ital.*, 1996, **126**, (9), 587–593

The complex (η^6 -naphthalene)(η^4 -COD)Ru(0) (COD = cycloocta-1,5-diene), in the presence of acetonitrile, readily catalyses the isomerisation of allyl ethers and allyl acetals to the corresponding vinyl derivatives, under mild conditions and in high yields. Supported and unsupported Ru aggregates are also active heterogeneous catalysts for these reactions.

Ruthenium-Catalyzed Oppenauer-Type Oxidation of 3 β -Hydroxy Steroids. A Highly Efficient Entry into the Steroidal Hormones with 4-En-3-one Functionality

M. L. S. ALMEIDA, P. KOČOVSKÝ and J.-E. BÄCKVALL, *J. Org. Chem.*, 1996, **61**, (19), 6587–6590

A mild and efficient process for the catalytic oxidation of 5-unsaturated 3 β -hydroxy steroids to the corresponding 4-en-3-one derivatives is reported using (PPh₃)₃RuCl₂ and K₂CO₃ or [(C₆H₅)₃COHOC(C₆H₅)₂(μ -H)][(CO)₂Ru₂] in acetone. The reactions proceed via a Ru-catalysed dehydrogenation of the steroid alcohol followed by H transfer to the acetone. No side reactions or decomposition products were detected.

Michael Reaction of Stabilized Carbon Nucleophiles Catalyzed by [RuH₂(PPh₃)₄]

E. GÓMEZ-BENGOA, J. M. CUERVA, C. MATEO and A. M. ECHAVARREN, *J. Am. Chem. Soc.*, 1996, **118**, (36), 8553–8565

The Michael reaction of active methylene compounds lacking cyano groups, such as malonates, β -ketoesters, etc., proceeds under mild and neutral conditions in acetonitrile solution in the presence of RuH₂(PPh₃)₄. Cyano acetates, more acidic than malonates in organic solvents, are also excellent substrates for this reaction. In a number of cases, intramolecular aldol reactions were also observed as side reactions.

A New Way for Efficient Catalysis by Using Low Valent Ruthenium Complexes as Redox Lewis Acid and Base Catalysts

S.-I. MURAHASHI and T. NAOTA, *Bull. Chem. Soc. Jpn.*, 1996, **69**, (7), 1805–1824

Divalent Ru dihydrides are excellent Lewis acid catalysts for the hydration of nitriles, amidation of amines and esterification of alcohols with nitriles. Thus, the hydration of acetonitrile at 120°C in the presence of 0.03 molar equivalents of RuH₂(PPh₃)₄ gives acetamide in 100% conversion and 92% yield. These complexes can also effect catalytic aldol-type reactions and Michael-type additions providing a novel and effective strategy for the catalytic C-C bond formation of nitriles under neutral and mild conditions.

FUEL CELLS

Electrochemical Oxidation of Methanol on Platinum Electrodes with Ruthenium Adatoms in Hot Phosphoric Acid

M. WATANABE, Y. GENJIMA and K. TURUMI, *Denki Kagaku*, 1996, **64**, (6), 462–463

An enhancement of Pt electrocatalytic activity by Ru ad-atoms for MeOH oxidation, and the preparation and activity of highly dispersed Pt-Ru alloy supported on C black in a conventional low temperature region, are reported. A higher temperature operation of > 100°C for DMFCs is advantageous with hot H₃PO₄ electrolyte and the increase of Pt(subs) by the Ru ad-atoms predicts the optimum activity for Ru-Pt alloys under the operating conditions.

MEDICAL USES

Electrochemical Determination of Carboplatin in Serum Using a DNA-Modified Glassy Carbon Electrode

A. M. O. BRETT, S. H. P. SERRANO, T. A. MACEDO, D. RAIMUNDO, M. H. MARQUES and M. A. LA-SCALEA, *Electroanalysis*, 1996, **8**, (11), 992–995

An electrode for the detection of the anticancer Pt drug carboplatin in serum samples of patients undergoing treatment for ovarian cancer is described. It shows that, for low concentrations, carboplatin interacts preferentially with adenine rather than guanine groups in the DNA. The detection limit was 5.7 × 10⁻⁶ M.