

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Optical Properties of Platinum Particles Synthesized in Microemulsions

J. F. RIVADULLA, M. C. VERGARA, M. C. BLANCO, M. A. LÓPEZ-QUINTELA and J. RIVAS, *J. Phys. Chem. B*, 1997, **101**, (44), 8997–9004

Nanoparticles (~4 nm) of Pt, synthesised from H₂PtCl₆ and hydrazine in water-in-oil microemulsions, show a maximum in optical absorption at 220–256 nm, depending on the reaction medium. Ageing of the solutions changed the optical properties due to cluster formation, as did heating without hydrazine. This colloidal Pt formation was catalysed by light.

Structure Sensitivity of Methane Dissociation on Palladium Single Crystal Surfaces

K. KLIER, J. S. HESS and R. G. HERMAN, *J. Chem. Phys.*, 1997, **107**, (10), 4033–4043

Pd single crystals are active for the C-H bond dissociation of CH₄ at 400–600 K. Dissociation rates varied by an order of magnitude in the order Pd(111) < Pd(311) < Pd(679), while the activation energies ranged from 32–34 kJ mol⁻¹ for Pd(111) and Pd(311), to 44 kJ mol⁻¹ for Pd(679). Defects on the Pd(679) surface provide a driving force of 26 kJ mol⁻¹ compared to the smooth planar Pd(111) surface, and 22 kJ mol⁻¹ compared to Pd(311).

Effect of Sputtering Pressure of Pd Underlayer on the Perpendicular Magnetic Anisotropy in Co/Pd Multilayered Thin Films

H.-S. OH, B.-I. LEE and S.-K. JOO, *IEEE Trans. Magn.*, 1997, **33**, (5), 3655–3657

The magnetic properties of Co/Pd multilayers were found to depend on the sputtering pressure of the Pd underlayer. Perpendicular coercivity of the multilayers increased as the Pd underlayer deposition pressure increased from 6 to 25 mTorr, with the increment of the coercivity being larger for films with thinner Co sublayers. The interface anisotropy energy decreased from 0.390 to 0.255 erg cm⁻², due to interface roughening of the multilayers. The magneto-elastic effect contributes to the perpendicular anisotropy.

Microstructural Analysis of Pd/Pt/Au/Pd Ohmic Contacts to InGaP/GaAs

D. G. IVEY, R. ZHANG, Z. ABID, S. EICHER and T. P. LESTER, *J. Mater. Sci.: Mater. Electron.*, 1997, **8**, (5), 281–288

The microstructure of low resistance Pd/Pt/Au/Pd *p*-ohmic contacts to InGaP/GaAs heterofunction bipolar transistors was studied during annealing. The Pd and Pt reacted with the InGaP emitter layer and GaAs base layer to form (Pt,Pd)_x(In,Ga)_{1-y}P (0 ≤ *x*, *y* ≤ 1), PtAs₂ and PdGa. Minimum values of 0.10–0.12 Ω mm were achieved after annealing at 415–440°C for contacts both with and without Zn.

CHEMICAL COMPOUNDS

Bi:RhBr₃: A Subbromide with Molecular [RhBiBr₃] Clusters

M. RUCK, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, (18), 1971–1973

The halogen-rich Bi subbromide Bi:RhBr₃, which consists of discrete molecular clusters of [RhBiBr₃], is reported. In this novel cluster, the Bi atoms are arranged as a pentagonal bipyramid around the central Rh atom, and the [RhBr₃] core is then surrounded by a distorted, square Br₄ antiprism. This is in contrast to currently known metal-rich Bi subiodides.

Room-Temperature Molten Salts of Ruthenium Tris(bipyridine)

H. MASUI and R. W. MURRAY, *Inorg. Chem.*, 1997, **36**, (22), 5118–5126

Attaching poly(ethylene glycol)-mono(methyl ether) (MePEG; MW = 350) chains to [Ru(bpy)₃]²⁺ complexes via 4,4'-bipyridine ester linkages produced room temperature, highly viscous, molten salts of the form [Ru(bpy)₃(bpy(CO.MePEG-350)_N)](ClO₄)₂ (*N* = 0, 1 and 2). Data are given for the adiabatic Ru(III/II) and Ru(II/I) electron self-exchange reaction rates in the pure melts.

Reactivity of Ru(H)(H₂)Cl(PCy₃)₂ with Propargyl and Vinyl Chlorides: New Methodology to Give Metathesis-Active Ruthenium Carbenes

T. E. WILHELM, T. R. BELDERRAIN, S. N. BROWN and R. H. GRUBBS, *Organometallics*, 1997, **16**, (18), 3867–3869

The reaction of [RuCl₂(COD)]₂, PCy₃, H₂ and NEt₃ in *sec*-butyl alcohol gave Ru(H)(H₂)Cl(PCy₃)₂ in 95% yield. Following a novel insertion-elimination pathway, this hydride can react with propargyl or vinyl halides to make metathesis-active vinyl and alkyl carbene species with the formulae (PCy₃)₂Cl₂Ru=CH-CH=CR₂ and (PCy₃)₂Cl₂Ru=CHR, respectively, with tertiary propargyl chlorides giving very high yields.

ELECTROCHEMISTRY

Carbon Monoxide Electrooxidation on Porous Pt-Ru Electrodes in Sulphuric Acid

A. S. ARICO, E. MODICA, E. PASSALACQUA, V. ANTONUCCI and P. L. ANTONUCCI, *J. Appl. Electrochem.*, 1997, **27**, (11), 1275–1282

The electrooxidation of CO on a Pt-Ru/C catalyst was studied in H₂SO₄ electrolyte. The apparent activation energy decreased with the increase of overpotential vs. NHE. The reaction order with respect to CO increased from 0.4 to 1, as the overpotential increased from 0.5 to 0.7 V vs. NHE, and a reaction order close to -1 with respect to the protonic concentration was observed.

A New Hydrogenation System of 4-Methylstyrene Using a Palladinized Palladium Sheet Electrode

C. IWAKURA, Y. YOSHIDA and H. INOUE, *J. Electroanal. Chem.*, 1997, **431**, (1), 43–45

A new palladinisation method has been developed in which active H₂ is passed through a Pd sheet electrode to form 3-dimensional Pd black deposits with a coral-like shape and a particle size < 1 μm. Using this palladinised Pd sheet electrode, the rate of 4-methylstyrene hydrogenation increased > 40 times, to give 4-ethyltoluene at the rate of 0.92 mmol h⁻¹. The marked increase in the hydrogenation rate was suggested to be due to an increase in the reaction zone and the appearance of new active sites.

Electrochemical Oxidation and Reduction of Rhodium and Iridium Complexes with Fullerenes C₆₀ and C₇₀

L. I. DENISOVICH, S. M. PEREGUDOVA, A. V. USATOV, A. L. SIGAN and Y. N. NOVIKOV, *Izv. RAN, Ser. Khim.*, 1997, (7), 1308–1313

Electrochemical studies on Rh and Ir complexes of the fullerenes C₆₀ and C₇₀ showed that they are capable of oxidation and reduction. The metallo-fullerene complexes were generated in situ from the interaction of C₆₀ and C₇₀ with Rh and Ir hydridocarbonyl phosphine complexes, HM(CO)(PPh₃)₃. The effect of the structure and CO₂ on the redox properties of fullerene complexes is discussed.

Dip-Coated Ru-V Oxide Electrodes for Electrochemical Capacitors

Y. TAKASU, T. NAKAMURA, H. OHKAWAUCHI and Y. MURAKAMI, *J. Electrochem. Soc.*, 1997, **144**, (8), 2601–2606

Dip-coated RuO₂-VO_x electrodes were prepared and found to have a large electrochemically active surface area, with an electrode of RuO₂(33%)-VO_x(67%)/Ti calcined at 450°C having the highest voltammetric charge of ~ 50 times that of a RuO₂/Ti electrode. This large surface area is characterised by the dispersion of fine V₂O₅ particles, the formation of Ru₂VO₆ and the probable presence of ultrafine RuO₂. The voltammetric charge of the electrode of 162 mC cm⁻² at 0.3–1.1 V at a sweep rate of 50 mV s⁻¹ corresponds to 0.76 protons contributed to the adsorption on every Ru ion.

Porous Ruthenium Oxide Electrode Prepared by Adding Lanthanum Chloride to the Coating Solution

Y. MURAKAMI, T. KONDO, Y. SHIMODA, H. KAJI, X.-G. ZHANG and Y. TAKASU, *J. Alloys Compd.*, 1997, **261**, 176–181

Porous RuO₂/Ti electrodes were prepared from RuO₂-La₂O₃/Ti (Ru:La = 7:3) electrodes by the complete dissolution of La ions in H₂SO₄, from the well complexed Ru-La oxide. The voltammetric charges of these electrodes were ~ 20 times larger than those of conventional RuO₂/Ti electrodes prepared by the thermal decomposition method.

PHOTOCONVERSION

Photochemistry of M(PP₃)H₂ (M = Ru, Os; PP₃ = P(CH₂CH₂PPh₂)₃): Preparative, NMR, and Time-Resolved Studies

R. OSMAN, D. I. PATTISON, R. N. PERUTZ, C. BIANCHINI, J. A. CASARES and M. PERUZZINI, *J. Am. Chem. Soc.*, 1997, **119**, (36), 8459–8473

Ru(PP₃)H₂ and Os(PP₃)H₂ were prepared and their photochemistry studied by various techniques. Key features include: the scavenging of N₂ by the cyclometallation product of Ru(PP₃); the totally different kinetic selectivity of Ru(PP₃) and Os(PP₃) compared with Ru(dppe)₂; the enhanced reactivity of Ru(PP₃) towards benzene and HSiEt₃; and the insertion of Os(PP₃) into aliphatic C-H bonds of THF and alkanes.

The Photovoltaic Stability of Bis(isothiocyanato)ruthenium(II)-bis-2,2'-bipyridine-4,4'-dicarboxylic Acid and Related Sensitizers

O. KOHLE, M. GRÄTZEL, A. F. MEYER and T. B. MEYER, *Adv. Mater.*, 1997, **9**, (11), 904–906

Endurance tests are reported for sealed photovoltaic cells with *cis*-Ru^{II}(LH₂)₂(NCS)₂ (LH₂ = 2,2'-bipyridyl-4,4'-dicarboxylic acid) as sensitiser. After > 7000 h of illumination with visible light at 1000 W m⁻² light intensity, the performance was unchanged. This was due to the speed of the interfacial redox processes during photovoltaic operation. They conclude that the electrolyte in solar cells should contain high iodide concentrations and not dissolve the sensitiser.

Photo- and Thermo-Chromism of a Ruthenium(II) Complex and Viologen-Containing Polymer Film

M. SUZUKI, M. KIMURA, K. HANABUSA and H. SHIRAI, *Chem. Commun.*, 1997, (21), 2061–2062

A polymer film comprising a Ru(II) complex and a viologen-containing partially quaternised poly(1-vinylimidazole) film is described. Upon light irradiation in air, the film colour changed from orange to blue, then reverted to orange on standing in the dark. Similar changes occurred upon heating (blue) and cooling (orange). Blue to orange changes were slower. The blue colour is due to the formation of viologen radicals formed by electron transfer from the photoexcited Ru(II) complex to the viologen.

Chemiluminescence in the Oxidation of Sodium Anthracenide and Pyrenide by Ru^{III} Complex

R. G. BULGAKOV and B. A. TISHIN, *Izv. RAN, Ser. Khim.*, 1997, (3), 609–611

Chemiluminescence (CL) during the oxidation of Na organocompounds (Na⁺R⁻) (R = anthracene or pyrene) in THF by Ru(bpy)₃²⁺ (1) has been studied. Using CL emitters, excited singlet states of polycyclic aromatic hydrocarbons 'R' (2) and Ru(bpy)₃²⁺ (3) were identified and a mechanism for their formation was proposed. It is suggested that (3) can be formed by reacting Ru(bpy)₃²⁺ with Ru(bpy)₃¹⁺ or by energy transfer from (2) to (1).

ELECTRODEPOSITION AND SURFACE COATINGS

Mesoporous Platinum Films from Lyotropic Liquid Crystalline Phases

G. S. ATTARD, P. N. BARTLETT, N. R. B. COLEMAN, J. M. ELLIOTT, J. R. OWEN and J. H. WANG, *Science*, 1997, **278**, (5339), 838–840

Pt was electrodeposited onto polished Au from a liquid crystalline plating mixture consisting of ternary systems of a non-ionic surfactant, such as octaethyleneglycolmonohexadecyl ether, H_2PtCl_6 and H_2O at 25–65°C. The surfactant was removed with deionised H_2O . Transmission electron micrographs showed Pt films consisting of a uniform highly porous hexagonal lattice structure with cylindrical holes. The diameter of the holes can be controlled either by changing the chain length of the surfactant or by adding a hydrophobic additive to the plating mixture.

Fabrication of Epitaxial Diamond Thin Film on Iridium

K. OHTSUKA, H. FUKUDA, K. SUZUKI and A. SAWABE, *Jpn. J. Appl. Phys., Part 2*, 1997, **36**, (9A/B), L1214–L1216

Smooth diamond thin films were epitaxially grown on a (001) Ir surface in a two-step direct current plasma CVD process, using ion irradiation pretreatment and diamond growth. The epitaxial areas of the diamond films, with a mean thickness of ~1.5 μm , acted as optical mirrors. The films had an average roughness of ~1 nm, a low C content, except for diamond, and an area of > 1 mm². The depth profiles of the thin films were studied using Confocal Raman spectroscopy.

APPARATUS AND TECHNIQUE

Photoluminescent Oxygen Sensing on a Specific Surface Area Using Phosphorescence Quenching of Pt-Porphyrin

S.-K. LEE and I. OKURA, *Anal. Sci.*, 1997, **13**, (4), 535–540

An optical sensor for O_2 -pressure measurements was developed based on the phosphorescence quenching, by O_2 , of Pt octaethylporphyrin incorporated in polymer films. This sensor had a good operational stability and < 10% photobleaching even after storage for > 1 year in the absence of light at room temperature.

Comparison of the Gold Reduction and Stripping Processes at Platinum, Rhodium, Iridium, Gold and Glassy Carbon Micro- and Macrodisk Electrodes

A. M. BOND, S. KRATZIS, S. MITCHELL and J. MOCÁK, *Analyst*, 1997, **122**, (10), 1147–1152

The reduction of Au(III) and the oxidative stripping of Au in 0.1 M HCl + 0.32 M HNO₃ were studied at Pt, Rh, Ir, Au and glassy C disk electrodes. Pt was the best electrode material and a Pt disk electrode, 50 μm in diameter, generated a maximum (stripping) peak:reduction current ratio, with a sharp, symmetrical, and a very well defined Au oxidation signal.

Simultaneous Amperometric and Potentiometric Detection of Inorganic Anions in Flow Systems Using Platinum and Silver/Silver Chloride Electrodes

Z. CHEN and D. B. HIBBERT, *Anal. Chim. Acta*, 1997, **350**, (1–2), 1–6

An electrochemical detection system for inorganic ions in flow systems uses both amperometric Pt and potentiometric Ag/AgCl electrodes, coupled with ion chromatography. After separation by anion-exchange chromatography, Cl⁻, Br⁻, I⁻, SCN⁻ and S₂O₃²⁻ were determined potentiometrically with a detection limit of 1×10^{-5} M while, simultaneously, NO₂⁻, Br⁻, I⁻ and SCN⁻ were determined amperometrically with a detection limit of 1×10^{-6} M. Ion-interaction chromatography separated and detected Br⁻, NO₂⁻ and SCN⁻.

Improved Performances of InGaP Schottky Contact with Ti/Pt/Au Metals and MSM Photodetectors by (NH₄)₂S_x Treatment

C.-T. LEE, M.-H. LAN and C.-D. TSAI, *Solid-State Electron.*, 1997, **41**, (11), 1715–1719

Studies are reported on the effect of (NH₄)₂S_x treatment of InGaP on the high performance of GaAs metal-semiconductor-metal (MSM) photodetectors with InGaP buffer and capping layers. The surface states were reduced by S passivation which improved the InGaP Schottky contact with Ti/Pt/Au. The improved dark current and insensitive response with incident optical power were demonstrated by suitable process control of S passivation.

Hydrogen Gas Detection via Photothermal Deflection Measurement

K. KALLI, A. OTHONOS and C. CHRISTOFIDES, *Rev. Sci. Instrum.*, 1997, **68**, (9), 3544–3552

A thermal wave H₂ sensor containing a thin film polyvinylidene fluoride film coated with a thin Pd layer was examined by transverse optical beam deflection spectroscopy. The sensitivity to H₂ resulted from thermal boundary condition changes at the gas-film interface and depended upon the thermophysical properties of the gas. Concentration measurements of 0.1% H₂ in the presence of a balanced air mixture at room temperature indicated possible sensitivities approaching 100 ppm.

Electrocatalytic Oxidation and Flow Amperometric Detection of Hydrazine at an Electropolymerized 4-Vinylpyridine/Palladium Film Electrode

T. LI and E. WANG, *Electroanalysis*, 1997, **9**, (15), 1205–1208

Electropolymerisation of 4-vinylpyridine onto the surface of a glassy carbon electrode followed by electrodeposition of Pd onto the polymer modified electrode surface gave a poly(4-vinyl)pyridine/Pd film electrode used for the electrocatalytic detection of hydrazine. Compared with Pd/glassy C electrodes, this electrode displays improved mechanical stability and higher sensitivity with a detection limit of 0.026 ng at 0.5 V and a linear range of 0.2 μM to 1 mM.

Stabilization of an Osmium Bis-Bipyridyl Polymer-Modified Carbon Paste Amperometric Glucose Biosensor Using Polyethyleneimine

J. JEZKOVA, E. I. IWUOHA, M. R. SMYTH and K. VYTRAS, *Electroanalysis*, 1997, **9**, (13), 978-984

Biosensors were constructed by the immobilisation of a glucose oxidase/Os-bis-bipyridyl poly(4-vinylpyridine) polymer electrostatic complex within C paste electrodes, and used as amperometric glucose sensors in the presence or absence of a stabilised polyethyleneimine (PEI). The PEI enhanced the stability of the electrode and its sensitivity. The biosensors showed rapid response, improved substrate specificity, high affinity for glucose, renewable surface and a broad pH range of high sensitivity.

Screen-Printed Ruthenium Dioxide Electrodes for pH Measurements

R. KONCKI and M. MASCINI, *Anal. Chim. Acta*, 1997, **351**, (1-3), 143-149

Cheap, disposable potentiometric pH sensors based on RuO₂ have been prepared by a highly reproducible, simple, low temperature firing screen-printing method on plastic supports. Fast measurements were achieved with good sensitivity (51 mV/pH) in acidic and neutral solutions with a linear range of response up to pH 8. There was also no interference from alkaline cations, common anions and complexing ligands, but the pH measurements were strongly affected by the presence of reducing compounds.

Immobilization of Ruthenium Tris-Bipyridyl Complex for Chlorine Gas Detection

T. E. BROOK and R. NARAYANASWAMY, *Sens. Actuators B, Chem.*, 1997, **38-39**, (1-3), 195-201

Methods for the physical immobilisation of a tris-bipyridyl Ru complex (Ru-TRL) have been examined for the use of TRL with a fibre-optic based sensing system for Cl₂(g). Polyvinyl pyrrolidone and silicone rubber matrices allowed rapid response to Cl₂ with detection limits of 0.675 and 1 ppm, respectively, under N₂. Silicone rubber showed a greater change in fluorescence intensity and speed of response and was less susceptible to humidity changes. Its detection limit, however, rose to 5 ppm in air.

Fabrication and Characterization of Ru-Doped TiO₂ Composite Membranes by the Sol-Gel Process

D.-S. BAE, K.-S. HAN and S.-H. CHOI, *Mater. Lett.*, 1997, **33**, (1, 2), 101-105

The effects of Ru on the grain growth, pore size and particle diameter of Ru doped TiO₂ composite membranes were studied on samples prepared by a sol-gel process. The doped TiO₂ sols were prepared by destabilisation of the colloidal solution process. The thickness of the doped membranes was 50-1000 nm, with a crack-free microstructure and narrow particle size distribution even after calcination at ≤ 800°C. The mean particle size of the Ru doped membrane was smaller than that of the undoped TiO₂ membrane.

HETEROGENEOUS CATALYSIS

Characteristics of Pt/H-beta and Pt/H-Mordenite Catalysts for the Isomerization of n-Hexane

J.-K. LEE and H.-K. RHEE, *Catal. Today*, 1997, **38**, (2), 235-242

Bifunctional Pt/H-beta (1) and Pt/H-MOR catalysts were prepared under various pretreatment conditions and tested in the isomerisation of n-hexane. (1) gave a higher yield of high octane dimethylbutanes and greater selectivity than the commercial Pt/H-MOR. This was because a larger number of acid sites were available to bulky reaction intermediates and the Pt clusters were well dispersed to give a proper balance between metallic centres and acid sites in (1).

Catalytic Removal of Nitric Oxide with Hydrogen and Carbon Monoxide in the Presence of Excess Oxygen

K. YOKOTA, M. FUKUI and T. TANAKA, *Appl. Surf. Sci.*, 1997, **121/122**, 273-277

The removal of NO_x with H₂ in the presence of excess O₂ was studied over Pt catalysts. Pt/zeolite had a high conversion efficiency but was readily poisoned by CO and hydrocarbons (HCs) and formed N₂O as a by-product. Reducing the oxidation efficiency of Pt gave an improved catalyst, Pt-Mo-Na/SiO₂, which has a higher temperature range of NO_x conversion, forms less N₂O and removes NO_x with HCs, H₂ and CO.

Investigation on Active Sites in Pt-Mo on Silica Catalysts for Reactions of Hydrocarbons with Hydrogen

G. LECLERCQ, S. PIETRZYK, T. ROMERO, A. EL GHARBI, L. GENGEMBRE, J. GRIMBLOT, F. AÏSSI, M. GUELTON, A. LATEF and L. LECLERCQ, *Ind. Eng. Chem. Res.*, 1997, **36**, (10), 4015-4027

Physico-chemical studies were performed on Pt-Mo/SiO₂ catalysts with the same (Pt + Mo) metal atom content but various Mo:Mo + Pt ratios. Pt was completely reduced to metal in H₂ at 400-700°C, independent of the reduction temperature, but only a fraction of Mo was reduced, depending on temperature. Two types of reaction occurred: cyclohexane dehydrogenation, alkane isomerisation and cyclisation, with the rate determining step occurring on Pt; and alkane hydrogenolysis, faster on Pt-Mo than on Pt, due to preferential adsorption on Pt-Mo sites.

Hydrogen Cyanide Synthesis on Polycrystalline Platinum and 90 : 10 Platinum-Rhodium Surfaces

A. BOCKHOLT, I. S. HARDING and R. M. NIX, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, (21), 3869-3878

HCN has been synthesised from CH₄-based feedstocks at relatively low temperatures (≤ 780°C) and pressures (0.02-0.15 Torr) over pure Pt and Pt-10%Rh alloy model catalysts. Maximum activity was observed for CH₄-NH₃-O₂ in a 1:1:0.5 ratio over Pt. Rh inhibited HCN production and Pt-10%Rh alloy gave lower HCN yield and selectivity.

Study on Catalysts for Methanol-Fuelled Vehicle Exhaust Control. I. Influence of Oxygen Content on Methanol Deep Oxidation over Pd/ γ -Al₂O₃

B. ZHU and R. WANG, *Chinese J. Catal.*, 1997, **18**, (5), 414–417

Studies on the effect of O₂ content on MeOH deep oxidation over Pd/ γ -Al₂O₃ showed that when Pd is present in a reduced state on the support, the MeOH oxidation activity and deep oxidation selectivity of the catalyst increase with increasing O₂ content. However, when the amount of O₂ increases to the extent that the Pd is transformed into an oxidised state, the activity and selectivity decrease. MeOH oxidation to formaldehyde was easier over Pd-O.

Preparation of Palladium Colloids in Block Copolymer Micelles and Their Use for the Catalysis of the Heck Reaction

S. KLINGELHÖFER, W. HEITZ, A. GREINER, S. OESTREICH, S. FÖRSTER and M. ANTONIETTI, *J. Am. Chem. Soc.*, 1997, **119**, (42), 10116–10120

Highly stable colloidal dispersions of nanometre sized Pd colloids have been prepared in block copolymer micelles of polystyrene-*b*-poly-4-vinylpyridine. These polymer/metal hybrids can be readily dissolved and handled in organic solvents and were successfully used for the Pd-catalysed C-C coupling of aryl halides with alkenes (Heck reaction). They showed similar reactivity to the low molecular weight Pd complexes traditionally used, but were far more stable, remaining catalytically active even after 50,000 turnover cycles without Pd black formation; thus the products may be suitable for pharmaceutical and electro-optical use.

Rh/One-Atomic Layer GeO₂/SiO₂ as a New Catalyst for Ethyl Acetate Hydrogenation at a Low Pressure

K. OKUMURA, K. ASAKURA and Y. IWASAWA, *Chem. Lett. Jpn.*, 1997, (10), 985–986

Rh₆(CO)₁₆ precursor was supported on one-atomic layer GeO₂/SiO₂ to give, after reduction at 423–523 K, a new Rh/one-atomic layer GeO₂/SiO₂ catalyst. This was active for the selective ($\leq 80\%$) hydrogenation of ethyl acetate to EtOH under mild reaction conditions (473 K; P(H₂) = 6.6 kPa), whereas Rh/bulk-GeO₂ and Rh/SiO₂ were inactive for this reaction. The by-product acetaldehyde was produced at higher prerduction temperatures.

Synergism in the Reaction of CO with O₂ on Bimetallic Rh-Pd Catalysts Supported on Silica

P. ARAYA and V. DIAZ, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, (21), 3887–3891

The activity of Pd-Rh/SiO₂ catalysts, prepared by various methods, towards the oxidation of CO with O₂ was studied, and a synergistic effect was found to exist between the two metals when the catalysts were prepared by sequential impregnation. This effect was highly dependent on the pretreatment of the catalysts. The coexistence of oxidised Rh and reduced Pd was necessary for the synergistic effect to occur.

Catalytic Decomposition of N₂O over Supported Rhodium Catalysts: High Activities of Rh/USY and Rh/Al₂O₃ and the Effect of Rh Precursors

K. YUZAKI, T. YARIMIZU, S.-I. ITO and K. KUNIMORI, *Catal. Lett.*, 1997, **47**, 173–175

The catalytic decomposition of N₂O to N₂ and O₂ was studied over supported Rh catalysts. Rh/Al₂O₃ and Rh/USY zeolite catalysts prepared from Rh(NO₃)₃ had higher activities than the previously reported Rh/ZSM-5 and Rh/ZnO. Rh/USY(NO₃)₃ was the most active with a TOF of $26.0 \times 10^3 \text{ s}^{-1}$. The activity of Rh/Al₂O₃ was far lower when prepared from RhCl₃, despite high dispersion of the Rh, probably due to residual Cl in the catalyst.

Hydroformylation of Hex-1-ene in the Presence of Rhodium Carbonyl Catalysts Immobilised on Polymeric Organosiloxanes

N. V. KOLESNICHENKO, G. V. TEREKHOVA, A. T. TELESHEV, E. I. ALEKSEEVA and E. V. SLIVINSKY, *Izv. RAN, Ser. Khim.*, 1997, (6), 1155–1157

Hydroformylation of hex-1-ene was catalysed by acacRh(CO)₂ immobilised on highly active and stable polymeric organosiloxanes. The effects of the nature of the oligomers, the oligomer ratio and the Rh:oligomer ratio in the polymer on the synthesis and catalytic properties of this system were investigated.

Catalysis by Polymer-Bound Rh₆ Carbonyl Clusters. Selective Hydrogenation of Carbonyl Compounds in the Presence of CO and H₂O

T. MIZUGAKI, K. EBITANI and K. KANEDA, *Appl. Surf. Sci.*, 1997, **121/122**, 360–365

The treatment of Rh₆(CO)₁₆ with functionalised polystyrenes gave polymer-bound Rh₆ cluster complexes which showed high catalytic activity for the hydrogenation of various aldehydes to the corresponding alcohols. The activity depended on the length of the spacers and on the basicity and hydrophilicity of the polymers. These reactions took place in a triphase system of H₂O, organic phase and polymer which simplifies work-up procedures.

Hydrogenation Isotherms of Adsorbed Carbon Species on a Ru/Al₂O₃ Catalyst after CO Adsorption and CO/H₂ Reaction

H. AHLAFI, M. NAWDALI, A. K. BENCHEIKH and D. BIANCHI, *Bull. Soc. Chim. Belg.*, 1997, **106**, (5), 245–252

Studies of the surface adsorbed C species formed on a 3.5% Ru/Al₂O₃ catalyst after chemisorption of either CO or CO/H₂ at 478 K are reported. Exposure to CO/He resulted in rapid formation of various adsorbed species on the Ru and the Al₂O₃. The transient isothermal hydrogenation to CH₄ showed three species: linear, bridged and gem-dicarbonyl CO species on the Ru particles. Some adsorbed CO species on the metal and a carbonate on the support are not hydrogenated to methane. Linear CO is the main adsorbed species on the surface. Exposure to CO/H₂ gave the same species, except the gem-dicarbonyl and carbonate. Some C₂H₄ species formed on the Ru surface and a formate species formed on the support.

HOMOGENEOUS CATALYSIS

Palladium-Catalyzed Amidocarbonylation – A New, Efficient Synthesis of *N*-Acyl Amino Acids

M. BELLER, M. ECKERT, F. VOLLMÜLLER, S. BOGDANOVIC and H. GEISLER, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, (13/14), 1494–1496

Pd halides have been shown to catalyse amidocarbonylation reactions under mild reaction conditions of 80°C and 10 bar CO. Pd(II) bromide was the most active, giving the highest ever turnover number of 25,000 (mol product per mol Pd-cat) and turnover frequency of > 400 (mol product per mol Pd-cat per hour) seen for this reaction. This system can also produce, in good yield, a much wider range of *N*-acyl amino acids than with Co catalysts.

Transition Metal Catalysis in Fluorous Media: Practical Application of a New Immobilization Principle to Rhodium-Catalyzed Hydroboration

J. J. JULIETTE, I. T. HORVÁTH and J. A. GLADYSZ, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, (15), 1610–1612

The “Teflon greaseball” catalyst $[\text{RhCl}\{\text{P}[\text{CH}_2\text{CH}_2(\text{CF}_2)_2\text{CF}_3]\}_2]$ (1) was prepared from $[\{\text{RhCl}(\text{cod})\}_2]$ and $\text{P}[\text{CH}_2\text{CH}_2(\text{CF}_2)_2\text{CF}_3]$, in 94 % yield. The catalyst is highly soluble in $\text{CF}_3\text{C}_6\text{F}_{11}$ and catalyses a variety of organic transformations. For hydroboration reactions, catalyst loadings of 0.01–0.25 mol% were effective under mild conditions (25–40°C, 1–40 h) giving turnover numbers of ~ 8500, high yields and good enantioselectivity. Products can be extracted with organic solvents, and the solution of (1) reused.

Catalytic Asymmetric Hydrosilylation with (Triazolinylidene)rhodium Complexes Containing an Axis of Chirality

D. ENDERS, E. GIELEN and K. BREUER, *Tetrahedron: Asymmetry*, 1997, **8**, (21), 3571–3574

Chiral (triazolinylidene)rhodium complexes have been synthesised with a diastereomeric excess of *de* = 91–97%. They are effective for the asymmetric hydrosilylation of methyl ketones giving alcohols with enantiomeric excesses of ≤ 44% and ≤ 90% yield. The selectivity was dependent on reaction temperature and the substituents on the chiral ligand, but independent of the reaction time or amount of catalyst. Yields however were dependent on the latter two conditions.

Hydrogenation of Phenylacetylene Catalyzed by a Dihydridorhodium Complex, $[\text{RhH}_2(\text{Ph}_2\text{N}_3)(\text{PPh}_3)_2]$

N. KAMEDA, Y. HASEGAWA and T. YONEDA, *Nippon Kagaku Kaishi*, 1997, (8), 560–564

The homogeneous hydrogenation of phenylacetylene was performed in the presence of $[\text{RhH}_2(\text{Ph}_2\text{N}_3)(\text{PPh}_3)_2]$ catalyst under 1 atm H_2 . Phenylacetylene was reduced to styrene in toluene with the catalytic activity reduced by increasing reaction temperature and the addition of triphenylphosphine or 1,3-diphenyltriazenes. Internal alkynes were not hydrogenated.

Synthesis and Catalytic Application of $[\text{Rh}(\text{PPh}_3)_2([\text{9}]\text{aneS}_3)]\text{PF}_6$

A. F. HILL and J. D. E. T. WILTON-ELY, *Organometallics*, 1997, **16**, (21), 4517–4518

The reaction of $[\text{RhCl}(\text{PPh}_3)_3]$ with $[\text{9}]\text{aneS}_3$ (1,4,7-trithiacyclononane) and NH_4PF_6 gave $[\text{Rh}(\text{PPh}_3)_2([\text{9}]\text{aneS}_3)]\text{PF}_6$ (1) which undergoes a range of ligand substitution and oxidative-addition reactions. (1) also effectively catalyses the demercuration of bis-(alkynyl)mercurials giving the product in 94% yield, which is higher than obtained with the conventional catalysts $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$ and $[\text{RhCl}(\text{PPh}_3)_3]$.

Asymmetric Transfer Hydrogenation Catalyzed by Diamine-Iridium(I) Complexes

S.-I. INOUE, K. NOMURA, S. HASHIGUCHI, R. NOYORI and Y. IZAWA, *Chem. Lett. Jpn.*, 1997, (9), 957–958

A series of Ir(I) catalysts was prepared from $[\text{IrCl}(\text{cod})_2]$ and chiral 1,1-di(*p*-anisyl)ethylenediamine derivatives and used for the asymmetric transfer hydrogenation of a range of aromatic ketones in 2-propanol. Good yields of ≤ 97% and enantioselectivities of ≤ 93% were observed in the presence of KOH at room temperature, comparable to enantioselectivities obtained by Rh(I) and Ru(II) catalysts.

ELECTRICAL AND ELECTRONIC ENGINEERING

Synthesis of the PZT Films Deposited on Pt-Coated (100) Si Substrates for Nonvolatile Memory Applications

A. KUMAR, M. R. ALAM, A. MANGIARACINA and M. SHAMSUZZOHA, *J. Electron. Mater.*, 1997, **26**, (11), 1331–1334

The growth of ferroelectric lead zirconate titanate (PZT) films deposited on Pt-coated (100) Si substrate by the pulsed laser deposition technique was studied using various deposition conditions. The best crystalline structure was observed for PZT deposited at 575°C in 450 m Torr O_2 partial pressure. The remnant polarisation and the retained polarisation of the ferroelectric capacitors were 13 and 20 $\mu\text{C cm}^{-2}$, respectively.

Oxygen Diffusion in Pt Bottom Electrodes of Ferroelectric Capacitors

Y. MATSUI, M. SUGA, M. HIRATANI, H. MIKI and Y. FUJISAKI, *Jpn. J. Appl. Phys., Part 2*, 1997, **36**, (9A/B), L1239–L1241

Oxygen diffusion through the grain boundaries of Pt films during the crystallisation annealing of $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ (PZT) was studied for the stacked structure of PZT/Pt/TiN, using two Pt films with different structures. For the TiN film exposed to air after deposition, the Pt film consisted of polycrystalline grains with random orientation, while on the TiN film with Pt sputtered in vacuo the grains were columnar (111)-oriented with continuous grain boundaries normal to the substrate. Differences in the grain boundary structures determine the O_2 diffusion rate in Pt which was desirably lower on the film exposed to air.