

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Microstructure and Mechanical Properties of Sputtered Platinum Films

H. TOKURA, B. WINDOW, D. NEELY and M. SWAIN, *Thin Solid Films*, 1994, 253, (1-2), 344-348

The microstructure and mechanical properties of magnetron-sputtered Pt films deposited at low gas pressures of Ar and Xe on heated Si substrates were studied by XRD. The strain observed in Pt films is strongly dependent on deposition temperatures. Compressive stresses produced during deposition were greater for Ar-sputtered films, due to additional bombardment of the growing film by energetic Ar atoms from the cathode. Linewidths of the X-ray peaks are larger for Ar- than for Xe-sputtered films, since the films take in Ar. The strain in films deposited with Ar has a maximum at 100°C. There is a decrease in hardness with temperature for both films, but Ar-sputtered films are harder.

Adsorption of Nanometer-Sized Palladium Particles on Si(100) Surfaces

E. P. BOONEKAMP, J. J. KELLY and L. G. J. FOKKINK, *Langmuir*, 1994, 10, (11), 4089-4094

Polymer-stabilised Pd particles adsorbed on Si initiated the growth of electroless Ni. The effect of the polymer (poly(vinylpyrrolidone)) on the surface coverage is described. Pd particles adsorbed strongly on Si, but almost no adsorption was observed on SiO₂. The extreme substrate specificity of adsorption may be used for electroless deposition of metal patterns on semiconductor substrates. Electroless metal deposition from this electroless solution occurs only for $\Gamma_{Pd} < 1.5 \times 10^{15}$ atoms/cm², suggesting that a critical Pd particle density is needed for Ni deposition. By adjusting the polymer content of the sols the Pd concentration can be changed.

Changes in Crystallographic Orientation of Thin Foils of Palladium and Palladium Alloys after the Absorption of Hydrogen

A. L. CABRERA, E. MORALES-LEAL, J. HASEN and I. K. SCHULLER, *Catal. Lett.*, 1995, 30, (1-4), 11-23

Studies of the adsorption/absorption of H₂ at room temperature by Pd, 16%Ag-Pd (1) and 5%Ru-Pd (2) foils showed that H₂ readily diffused in the Pd and desorbed as one broad peak at ~ 650 K. H₂ also diffused in (1) and (2) foils but with a smaller diffusion constant. XRD studies of crystallographic orientation of the foils showed a preferential (1,1,0) orientation along the direction of rolling of the foils, which was destroyed after H₂ adsorption for Pd and (1) but unaltered for (2). This orientation of the foils could be important in membrane fabrication, since H₂ absorption by Pd is very dependent on surface orientation.

The Vibrational Excitations and the Position of Hydrogen in Nanocrystalline Palladium

U. STUHR, H. WIPF, T. J. UDOVIC, J. WEISSMÜLLER and H. GLEITER, *J. Phys.: Condens. Matter.*, 1995, 7, (2), 219-230

The solubility and vibrational modes of H in nanocrystalline Pd were studied at ≤ 4.8 at. % H and the locations of the H were determined. At room temperature, no precipitation of the H in a hydride phase (β -phase) was observed. Solubility measurements show enhanced H solubility relative to coarse-grained Pd. This additional H was incorporated in the grain boundaries and at the surface of the grains.

In situ Comparison of Diffusivities for Hydrogen and Deuterium in Palladium

C. J. LIHN, C. C. WAN and T. P. PERNG, *J. Appl. Electrochem.*, 1995, 25, (1), 61-67

The diffusion behaviour of H and D in Pd was studied by an electrochemical permeation method using solutions of 0.1 M LiOD (in D₂O) and 0.1 M LiOH (in H₂O) and their mixtures as the catholytes. The results showed that the effective diffusivities increased with the concentration of D in the electrolyte. Comparison of corresponding permeation transients showed higher diffusivity of D in Pd than H.

Surface Analysis of the PdCu(110) Single Crystal Alloy at Different Segregation Rates

J. LOBODA-CACKOVIC, M. S. MOUSA and J. H. BLOCK, *Vacuum*, 1995, 46, (2), 89-96

The PdCu(110) plane, with Pd : Cu = 1 : 1 in the bulk, was prepared with various surface compositions, by applying cycles of Ar ion sputtering and annealing at $420 < T_{AN} < 820$ K. A smooth Pd-rich surface was produced by high temperature treatment of the surface followed by low temperature sputtering and annealing at T_{AN} below that of Cu segregation, ~ 550 K. A large number of sputtering and annealing cycles without prior high T_{AN} gave a rough surface, which allowed Cu atoms lying beneath the surface to react.

Transmission Electron Microscopy and X-ray Diffraction Investigation of Phase Formation and Transition between Pd₂Si and PdSi in Pd Thin Films on (111)Si

J. F. CHEN and L. J. CHEN, *Mater. Chem. Phys.*, 1995, 39, (2), 229-235

Studies of the phase formation and transition between Pd₂Si and PdSi in Pd thin films on (111)Si showed that in as-deposited and 200°C/1 h annealed Pd(30 nm)/(111)Si samples, epitaxial Pd₂Si coexisted with the unreacted Pd layer. At annealing temperatures 250-800, 850 and 900-1000°C, only epitaxial Pd₂Si, PdSi and Pd₃Si phases, and mainly Pd₂Si and PdSi, were found, respectively. Pd₂Si and PdSi were the stable phases at 300-800 and 850-875°C, respectively.

Heat of Crystallization and Microstructure of Amorphous Pd₈₂Si₁₈ and Fe₈₀B₂₀ Alloys

E. ASAYAMA, H. IMAMURA, H. TAKEBE and K. MORINAGA, *Mater. Trans., JIM*, 1994, **35**, (10), 708–715

The correlation between the heat of crystallisation (1) and microstructure of Pd₈₂Si₁₈ and Fe₈₀B₂₀ alloys was studied on alloys prepared by a melt-spinning method with various rotating velocities of the Cu wheel. X-ray amorphous Pd₈₂Si₁₈ alloy, whose XRD pattern showed a halo, had a uniform microstructure without crystals, that is glass. The critical cooling rate for the formation of the X-ray amorphous phase in Pd₈₂Si₁₈ alloys is the minimum cooling rate to avoid detectable crystal formation. (1) is proposed as a parameter of the degree of non-crystallinity for the alloys.

Bulk Nanophase Pd₈₂Si₁₈ Directly Synthesized by High Pressure Quenching from Melt of Alloy

Z.-C. QIN, Y. LIU, Y. ZHANG, W. LIU and W.-K. WANG, *J. Mater. Sci. Lett.*, 1995, **14**, (3), 209–210

Bulk nanophase Pd₈₂Si₁₈ was prepared directly by quenching the melt of the alloy to room temperature under high pressure. The matrix alloy was prepared by arc-melting a mixture of pure Pd and Si in an Ar atmosphere. Bulk nanophase metal or alloy was thus obtained without preparing ultrafine particles or atom clusters. Also, the original alloy need not transform into the amorphous state. There are no voids or small pores in the bulk nanophase materials prepared by this route, due to their direct synthesis from the melt. Pressure used during quenching is a most important factor in synthesising these materials.

Mechanism of Low-Temperature Rhodium Oxidation

A. N. SALANOV and V. I. SAVCHENKO, *Kinet. Katal.*, 1994, **35**, (5), 780–785

Interactions of O₂ with Rh(100) and polycrystalline Rh were studied at O₂ pressures of 10⁵–10³ Pa and 400–600 K. At O₂ pressure ≥ 10¹ Pa, a Rh₂O₃ layer was formed and its volume increased according to a mechanism of low-temperature oxidation of metals by Cabrera-Mott. The increase in the layer thickness depends on both the O₂ pressure and the temperature. The data show a weak structural effect from the Rh surface on the oxidation process.

Rhodium Segregation in Dilute Silver-Rhodium Alloys

K. KRÓLAS and M. STERNIK, *Acta Metall. Mater.*, 1995, **43**, (1), 51–57

Segregation of Rh in Ag-Rh alloys has been studied by perturbed angular correlation of γ -rays emitted in the nuclear decay of radioactive ¹¹¹In. The formation of impurity complexes, of an ¹¹¹In probe atom and one or more Rh atoms, was observed as a function of annealing time and temperature. Rh atoms starts to aggregate at ~ 600 K. The solute Rh atom concentration (1) depended on the nominal alloy concentration (2) and temperature. (1) increased as a function of (2) up to about 0.04 at.% and was then unchanged for 0.1–0.5 at.% Rh. (1) was 3 times larger at the melting point, 1234 K, than at 750 K.

Kondo Coherence Gap and Superconductivity in the Ce_{1-x}La_xRhSb System

S. K. MALIK, L. MENON, K. GHOSH and S. RAMAKRISHNAN, *Phys. Rev. B*, 1995, **51**, (1), 399–403

The gap formation in the electronic density of states in CeRhSb, a mixed valent Ce-based compound which undergoes a rapid rise in resistivity at low temperatures attributable to the gap opening, has been investigated by addition of La. The gap formation was rapidly suppressed on replacing a small amount of Ce by non-magnetic La, but susceptibility continued to show mixed-valent behaviour. With increased La concentration, the susceptibility of the compounds in the solid solution Ce_{1-x}La_xRhSb gradually changes from mixed-valent type to Curie-Weiss type.

Magnetic Properties of New M-Type Hexaferrites BaFe_{12-2x}Ir_xCo₂O₁₉

B. SUGG and H. VINCENT, *J. Magn. Magn. Mater.*, 1995, **139**, 364–370

M-type BaFe₁₂O₁₉ hexagonal ferrite powders with partial substitution x Ir³⁺ + x Co²⁺ for $2x$ Fe³⁺ were produced by sintering. The intrinsic uniaxial anisotropy becomes planar in the title compound for $x = 0.5$. The saturation magnetisation decreased linearly from 71.2 to 58.9 emu/g with increasing doping content of 0 to 0.8. The coercivity dropped sharply for $x = 0.3$ and the ordering temperature decreased linearly with increasing x . The substitution of $x = 0.6$ resulted in a material with planar anisotropy.

CHEMICAL COMPOUNDS

Synthesis and Properties of Platinum Complexes of Fullerenes (C₆₀ and C₇₀)

M. IYODA, Y. OGAWA, H. MATSUYAMA, H. UENO, K. KIKUCHI, I. IKEMOTO and Y. ACHIBA, *Fullerene Sci. Technol.*, 1995, **3**, (1), 1–9

Pt complexes of fullerenes were prepared by the reaction of C₆₀ and C₇₀ with (CH₂=CH₂)Pt(PPh₃)₂ or Pt(PEt₃)₄. The crude Pt complexes were dissolved in benzene-hexane (1) and purified by column chromatography on SiO₂ gel. Elution using (1) (1:2) gave the pure (Et₃P)₂Pt(η^2 -C₆₀) complex in 68% yield with 32% of recovered C₆₀. The X-ray data of the C₆₀-Pt complex showed definite bond lengths and angles.

The Extraordinary Properties of Electrochemically Synthesized Cluster Compound K_{1.64}Pt(C₂O₄)₂

L. XU and S. DONG, *Electrochim. Acta*, 1994, **39**, (17), 2599–2604

The conducting Pt cluster compound K_{1.64}Pt(C₂O₄)₂ (1) was synthesised on a glassy C electrode by electrooxidation of K₂Pt(C₂O₄)₂ by a single potential step and cyclic voltammetry. (1) is fibrous with excellent conductivity and is effective for the electroactive species in solution, since its plateau current has the same potential as the peak current. (1) can be used in organic films of chemically modified electrodes as a conductor. An ultramicro electrode could be made from a single crystal of (1), as it has linear crystal morphology and anisotropic conductivity.

Organometallic Hydrides as Reactants in Fullerene Chemistry. The Interaction of C₆₀ and C₇₀ Fullerenes with HIr(CO)(PPh₃)₃

A. V. USATOV, E. V. VORONTOV, L. E. VINOGRADOVA and YU. N. NOVIKOV, *Izv. Akad. Nauk, Ser. Khim.*, 1994, (9), 1661–1665

Ir hydride HIr(CO)(PPh₃)₃ reacted with fullerenes C₆₀ and C₇₀ yielding (η²-C_n)IrH(CO)(PPh₃)₂ (n = 60, 70) complexes. Their composition, configuration and position of a double bond in a fullerene moiety co-ordinated with Ir atom were studied by IR, to compare the deuterio forms, and by ¹H and ³¹P spectroscopies.

Preparations of Ultrafine IrO₂-SnO₂ Binary Oxide Particles by a Sol-Gel Process

Y. MURAKAMI, H. OHKAWAUCHI, M. ITO, K. YAHIKOZAWA and Y. TAKASU, *Electrochim. Acta*, 1994, **39**, (17), 2551–2554

Ultrafine particles of Ir (100%) and Sn (100%) oxides of homogeneous composition, and four IrO₂-SnO₂ binary oxides with different Ir:Sn atomic ratios, were prepared by a sol-gel process. The unit length of rutile-type (Ir, Sn)O₂ cell decreased with increasing Ir⁴⁺ content. The Ir-Sn binary oxides crystallised to the (Ir, Sn)O₂ rutile-type phase at a lower temperature than Ir oxide to IrO₂.

Osmium Carbonyl Cluster Growth on Self-Assembled (3-Mercaptopropyl)trimethoxysilane on a Gold Surface

A. MORNEAU, A. MANIVANNAN and C. R. CABRERA, *Langmuir*, 1994, **10**, (11), 3940–3942

The growth of an Os carbonyl cluster on a self-assembled alkylsiloxanethiol monolayer, (3-mercaptopropyl)trimethoxysilane (1) on a Au(111) surface was studied by observing the surface reaction of Os₃(CO)₁₁(NCCCH₃) with (1). The Os cluster reacted with (1) destroying the well-ordered thiol surface forming several cluster aggregates of 10–22% diameter.

Triosmium Cluster Derivatives of [60] Fullerene

J. T. PARK, J.-J. CHO and H. SONG, *J. Chem. Soc., Chem. Commun.*, 1995, (1), 15–16

Triosmium carbonyl cluster derivatives of [60]-fullerene, Os₃(CO)₁₁(η²-C₆₀), Os₃(CO)₁₀(NCMe)(η²-C₆₀), Os₃(CO)₁₀(PPh₃)(η²-C₆₀) and Os₃(CO)₉(PPh₃)₂(η²-C₆₀) were prepared. A definite structural assignment was made using spectroscopic data.

A Zwitterionic Cluster Compound: Synthesis and Characterisation of the Triphenylphosphoniocyclopentadienide Derivative [Ru₆C(CO)₁₄(η⁵-C₅H₄PPh₃)]

A. J. BLAKE, B. F. G. JOHNSON, S. PARSONS and D. S. SHEPHARD, *J. Chem. Soc., Dalton Trans.*, 1995, (3), 495–496

The octahedral cluster [Ru₆C(CO)₁₄(η⁵-C₅H₄PPh₃)] was prepared by the reaction of [Ru₆C(CO)₁₇] with trimethylamine N-oxide in the presence of C₅H₄PPh₃. Crystal and molecular structure studies showed that this Ru organocluster complex contains an apically co-ordinated cyclopentadienyl unit.

Photophysical Properties of Monomeric and Oligomeric Ruthenium(II) Porphyrins

M. IKONEN, D. GUEZ, V. MARVAUD and D. MARKOVITSI, *Chem. Phys. Lett.*, 1994, **231**, (1), 93–97

The photophysical properties of three Ru(II) porphyrins: RuTBP(CO)(EtOH) (1), RuTBP(py₂)₂ (2) and [RuTBP(py₂)]_n (3) where TBP = tetrakis(3,5-di-tert-butyl-4-hydroxyphenyl) porphyrin and py₂ = pyrazine, are discussed. The lowest excited state of (2) is the triplet metal-to-ring charge transfer having weak luminescence with quantum yield of 0.6 × 10⁻¹ and a lifetime of 51 ns. (3) behaves as “insulated wire” which is confirmed by the small Stokes shift associated with the CT emission.

ELECTROCHEMISTRY

Electropolymerization of 2-Hydroxy-3-Aminophenazine (HAPh): Properties of pHAPh Films and Kinetics of Oxidation and Incorporation of Dihydroxybenzenes at Pt/pHAPh Electrodes

G. KOKKINIDIS, A. PAPOUTSIS and I. POULIOS, *J. Electroanal. Chem.*, 1994, **379**, (1–2), 379–387

A stable redox active polymer (pHAPh) with structure and redox properties close to those of poly(o-phenylenediamine) and poly(o-aminophenol) was prepared after oxidative electropolymerisation of 2-hydroxy-3-aminophenazine (HAPh) on Pt, Au, glassy C and ITO electrodes. Rotating Pt/pHAPh disc electrode studies showed that dihydroxybenzenes were incorporated into the pHAPh film in the reduced state, but p-benzoquinone was added in its oxidised state.

Electro-Oxidation Mechanisms of Methanol and Formic Acid on Pt-Ru Alloy Surfaces

N. M. MARKOVIC, H. A. GASTEIGER, P. N. ROSS, X. JIANG, I. VILLEGAS and M. J. WEAVER, *Electrochim. Acta*, 1995, **40**, (1), 91–98

The extent of adsorbed CO produced at Pt, Ru and Pt-Ru alloy electrodes during MeOH and formic acid oxidation in acidic supporting electrolyte was studied by voltammetry and spectroscopy. The addition of ~10 at.% Ru to Pt decreased the quasi-steady-state level of adsorbed CO, at any potential, in either solution. This was even more pronounced for 50% Ru alloy, when the CO coverage was reduced to < 10%.

Palladium Metal Microparticles Incorporation in Poly (N-Substituted Pyrrole) Film-Coated Electrode

N. TAKANO, M. NAKABAYASHI and N. TAKENO, *Denki Kagaku*, 1994, **62**, (12), 1238–1239

Pd metal was incorporated into new poly (N-linear alkyl substituted pyrrole) film-coated electrodes by immersing the electrodes into Na₂PdCl₄ solution. The substituents were C₅H₁₁ (a), C₅H₁₀OH (b) and C₅H₁₀OMe (c). Current/voltage curves for H₂ evolution in the buffer showed that (a)/Pd and (c)/Pd electrodes had smaller changes in the cathodic current than did the (b)/Pd electrode, which had high H evolution currents at lower potentials and high stability.

Electrochemical Formation of Pd-Li Alloys in LiCl-KCl Eutectic Melts

T. NOHIRA, K. AMEZAWA and Y. ITO, *J. Appl. Electrochem.*, 1995, 25, (1), 48–53

Cyclic voltammetry, open-circuit potentiometry and XRD were used to examine the electrochemical formation of Pd-Li alloys and Pd-rare earth alloys via deposition of Li onto a Pd electrode in molten LiCl-KCl eutectic melts. Various Pd-Li alloy phases were formed, such as LiPd₇, LiPd₂₃, LiPd and Li₂Pd, at 1.05, 0.64, 0.53 and 0.20 V vs. Li⁺/Li at 450°C, respectively. The results provide data on the electrochemical window of the molten LiCl-KCl system for Pd-rare earth alloy electrochemical formation using Pd electrodes.

Cathodic Reduction of Nicotinamide Coenzyme (NAD⁺) Mediated with Rhodium Complex Immobilized on Electrode Surface

Y. SHIMIZU, A. KITANI, S. ITO and K. SASAKI, *Denki Kagaku*, 1994, 62, (12), 1233–1234

The reduction of NAD⁺, mediated with [Rh(bpy)₃]³⁺ complex immobilised on an electrode surface, was performed to obtain the highly selective regeneration of NADH. (1) was immobilised by ion-exchange onto the hydrogel coated electrode. The cathodic reduction of NAD⁺ was performed in a divided electrolysis cell in a buffer (pH = 8.0) containing 1 mM NAD⁺, using a Pt plate and a saturated calomel electrode as the counter and the reference electrodes, respectively. [Rh(bpy)₃]³⁺/hydrogel electrode used for repeated runs of NAD⁺ reduction showed excellent stability.

PHOTOCONVERSION

Photoreduction of Water by the System of C₆₀-Platinum-Methylviologen

M. IGARASHI, M. FUKUDA, M. TAKI, T. TAGO, T. MINOWA, Y. OKADA and J. NISHIMURA, *Fullerene Sci. Technol.*, 1995, 3, (1), 37–43

A fullerene-Pt-methylviologen photocatalytic system was used successfully to reduce H₂O under photoirradiation through a Pyrex filter. The light is absorbed by the photocatalyst, and the valence electron is lifted to the conduction band level and transferred to the methylviologen and then to colloidal Pt. At the Pt surface, H₂O is reduced by the electron. The maximum evolution of H₂ was 110 μmol/head space of 5 ml/5 h.

Surface States in the Band-Gap for Pt-Deposited p-InP Photoelectrochemical Cells

H. KOBAYASHI, F. MIZUNO and Y. NAKATO, *Appl. Surf. Sci.*, 1994, 81, (4), 399–408

The effect of surface states in the band-gap for Pt-deposited p-InP(100) photoelectrochemical cells on the cell performance was studied. The maximum of the surface state density was located at ~0.16 eV above the InP valence-band maximum and these states are in a negative or neutral charge state, depending on the electrode potential. An increase in the barrier height is nearly proportional to the decrease in the surface state density. The decrease of the photovoltage caused by lowering the barrier height in the p-InP is due to the static negative charge in the surface states.

Photogeneration of Hydrogen Using Visible Light with Undoped/Doped α-Fe₂O₃ in the Presence of Methyl Viologen

K. GURUNATHAN and P. MARUTHAMUTHU, *Int. J. Hydrogen Energy*, 1995, 20, (4), 287–295

Visible light-induced H₂ production from H₂O splitting reactions was studied by using undoped or Rh(III)/Cu(II)-doped, with or without RuO₂ loaded α-Fe₂O₃ at various pH, with methyl viologen as an electron relay. Loading with Rh(III) and Cu(II) ions increased the H₂ production efficiency of the photocatalyst, with Rh(III) being more effective than Cu(II) in increasing the photocatalytic activity of α-Fe₂O₃. The increased activity is explained via the role of the metal ions loaded in the photogenerated electron-hole separation. Simultaneous loading of RuO₂ and Rh(III)/Cu(II) ions further increased the efficiency.

Photocatalytic Reduction of Nitrogen over (Fe, Ru or Os)/TiO₂ Catalysts

N. N. RAO, S. DUBE and M. P. NATARAJAN, *Appl. Catal. B: Environ.*, 1994, 5, (1–2), 33–42

Irradiated aqueous suspensions of Ru, Os or Fe/TiO₂ catalysts were active for the photocatalytic reduction of N₂ to NH₃. The catalytic activity was in order Ru > Fe > Os, but the reverse order was found for the stability of the catalysts with respect to NH₃ formation. However, the catalysts appear to lose activity due to the disappearance of Ti³⁺ sites.

Ru(bpy)₃²⁺ Bound to an Insoluble Polymeric Phase. Reductive Luminescence Quenching

J. L. BOURDELANDE, J. FONT, G. MARQUÉS and D. SALVATIERRA, *J. Photochem. Photobiol. A: Chem.*, 1995, 85, (1–2), 143–145

The reductive quenching of excited Ru(bpy)₃²⁺ (bpy = bipyridyl) covalently bound to insoluble polystyrene showed two different polymeric environments and two different photochemical behaviours for the excited complex. It is concluded that only those Ru(bpy)₃²⁺ units linked to the surface of the bead (functional groups, up to 1.5%) can be deactivated by *N,N*-dimethylaniline by rapid reductive quenching after irradiation while the rest remain unavailable in the interior of the bead.

ELECTRODEPOSITION AND SURFACE COATINGS

Thermal Cycling of Iridium Coatings on Isotropic Graphite

K. MUMTAZ, J. ECHIGOYA, H. ENOKI, T. HIRAI and Y. SHINDO, *J. Mater. Sci.*, 1995, 30, (2), 465–472

Thermal cycling and long-term heat testing on Ir-coated isotropic graphite substrates showed variation in the surface morphology at 300–2173 K. The columnar structure was retained after thermal cycling at 300–1873 K, but this was replaced by dense equiaxed grains whose size increased with time and temperature at high-temperature thermal cycling or heating at 1873 K for 90 ks. The pores in the coating which appeared after thermal cycling at 300–1873 K diminished after high-temperature thermal cycling.

APPARATUS AND TECHNIQUE

Dry Etching of Palladium Thin Films in Fluorine Containing Plasmas: X-ray Photoelectron Spectroscopy Investigation

F. FRACASSI, R. D'AGOSTINO and A. CACUCCI, *J. Vac. Sci. Technol.*, 1995, **13**, (1), 63–66

The dry etching process of Pd thin films was studied in Ar-CF₄ and Ar-CF₄-O₂ glow discharges by performing etch rate measurements and XPS analyses. The etching process was physical sputtering; F atoms react with Pd forming a fluorinated layer, such as PdF, which has a lower sputtering rate than metallic Pd. By increasing the amount of O₂ in the feed gas the surface CF_x contamination is reduced, gas phase F atom concentration increases, but the etching rate remains ~ 8 times lower than that with 100% Ar.

Electrochemical and Mirage Detection Studies of Sputtered Iridium Oxide Films

M. BARDIN, P. LOHEAC, M. PETIT, V. PLICHON and N. RICHARD, *New J. Chem.*, 1995, **19**, (1), 59–63

Electrochemical measurements and ion flux detection on sputtered Ir oxide films (SIROFS) in contact with aqueous solutions of variable pH or neutral alkali electrolytes were carried out. The shape of the voltammograms was highly dependent on the electrolyte, changing from a capacitive response to a double-peak shape. The probe beam deflection technique (mirage effect) showed that capacitive voltammograms correspond to an H⁺ or HO⁻ exchange, while peak-shaped voltammograms display a complex double ion flux. The charge of the Ir oxide films is mainly faradaic, regardless of the voltammogram shape.

Os(phen)₂(dppz)³⁺: A Red-Emitting DNA Probe

R. E. HOLMLIN and J. K. BARTON, *Inorg. Chem.*, 1995, **34**, (1), 7–8

An Os bi(1,10-phenanthroline) dipyrido[3,2-*a*:2',3'-*c*]phenazine complex, Os(phen)₂dppz³⁺, was prepared and tested as a DNA probe. When DNA was present in solution with the Os complex, it emitted red light of λ 700–800 nm with lifetimes 10 ns, and could be used as a fast diagnostic DNA probe.

HETEROGENEOUS CATALYSIS

Catalytic Oxidation of Dichloromethane, Chloroform, and Their Binary Mixtures over a Platinum Alumina Catalyst

D. M. PAPANMEIER and J. A. ROSSIN, *Ind. Eng. Chem. Res.*, 1994, **33**, (12), 3094–3103

The complete catalytic oxidation of CH₂Cl₂ (1), CHCl₃ (2) and their mixtures in humid air was studied over a 3% Pt/ κ - δ Al₂O₃ catalyst in a fixed bed catalytic reactor at 300–400°C. The oxidation of (1) and (2) as pure compounds was non-linear in the concentration of (1) and zeroth order in the concentration of O₂. This was explained by the formation of HCl during the oxidation which decreased the reaction rate. The final reaction rate expressions can predict catalyst performance during the oxidation of (1):(2) mixtures.

The Influence of Sulfur Dioxide on Propane Oxidation Activity over Supported Platinum and Palladium

C. P. HUBBARD, K. OTTO, H. S. GANDHI and K. Y. S. NG, *Catal. Lett.*, 1995, **30**, (1–4), 41–51

Four catalysts, Pt/ γ -Al₂O₃, Pt/ZrO₂, Pd/ γ -Al₂O₃ and Pd/ZrO₂, were studied in order to compare the known effects of metal-support activity and sulphate on Pt, with Pd, for propane oxidation. Metal loading was \leq 0.05 wt.%. In contrast to Pt, sulphation did not promote propane oxidation on Pd/ γ -Al₂O₃, and Pd/ZrO₂ was less active than Pd/ γ -Al₂O₃. The acid strength of ZrO₂ was significantly increased after sulphation, while that of γ -Al₂O₃ was only slightly raised.

Investigation of Pt/Al₂O₃ and Pd/Al₂O₃ Catalysts for the Combustion of Methane at Low Concentrations

R. BURCH and P. K. LOADER, *Appl. Catal. B: Environ.*, 1994, **5**, (1–2), 149–164

Pt/Al₂O₃ and Pd/Al₂O₃ catalysts, prepared from Cl-free precursors, were studied during the combustion of CH₄ under lean, stoichiometric and rich conditions using dilute mixtures. Under lean conditions, and at low conversions under stoichiometric or rich conditions, Pd/Al₂O₃ was the more effective catalyst, but at higher conversions Pt/Al₂O₃ was more active. This change over is associated with a "light-off" effect observed with Pt/Al₂O₃. Pt can be a more effective catalyst than Pd for CH₄ combustion under real conditions for natural gas fuelled vehicles.

Metal-Support Interaction in Pt/C Catalysts. Influence of the Support Surface Chemistry and the Metal Precursor

M. C. ROMÁN-MARTÍNEZ, D. CAZORLA-AMORÓS, A. LINARES-SOLANO, C. SALINAS-MARTÍNEZ DE LECEA, H. YAMASHITA and M. ANPO, *Carbon*, 1995, **33**, (1), 3–13

The effect of support surface chemistry and metal precursor species on Pt/C properties was studied using the char of a phenolformaldehyde polymer as the C source and H₂PtCl₆ acid and [Pt(NH₃)₄]Cl₂ as precursors. The Pt precursor distribution on the supports, and the metal precursor-support interaction, depended on the support surface. The surface oxidation of the supports has a negative effect on the Pt dispersion. The lower the number of surface O complexes, the higher the metal dispersion.

Catalytic Behaviour of Carbon-Supported FeM (M = Ru, Pt) in Pyridine Hydrodenitrogenation

A. GUERRERO-RUIZ, A. SEPULVEDA-ESCRIBANO, I. RODRIGUEZ-RAMOS, A. LOPEZ-AGUDO and J. L. G. FIERRO, *Fuel*, 1995, **74**, (2), 279–283

C-supported one-component Fe, Ru and Pt, and two-component FeRu and FePt catalysts were used for hydrodenitrogenation of pyridine at 3.0 MPa and 573 K. Fe and Ru monocomponent catalysts were sulphided, but Pt partly preserved its metallic character. A decrease in the Fe:C ratio and a big increase in the Pt:C ratio in the two-component catalysts showed that Fe is redispersed during incorporation of Pt, and Pt is deposited mainly at the outer surface.

Performance and Durability of Pt-MFI Zeolite Catalyst for Selective Reduction of Nitrogen Monoxide in Actual Diesel Engine Exhaust

M. IWAMOTO, H. YAHIRO, H. KHIL SHIN, M. WATANABE, J. GUO, M. KONNO, T. CHIKAHISA and T. MURAYAMA, *Appl. Catal. B: Environ.*, 1994, 5, (1-2), L1-L5

Selective catalytic reduction of NO by hydrocarbon in an oxidising atmosphere was studied over Pt-MFI zeolite (Pt-MFI) in synthesised or actual diesel engine exhaust gases. The activity of Pt-MFI in the synthesised gas, containing 10% H₂O, changed in the early stage of use, but levelled off after 150-200 h, and then was constant for > 800 h. The Pt-MFI catalyst had stable activity at 423-773 K and 10,000-150,000/h (gas hourly space velocity) in actual engine exhaust with light oil as a fuel. The amount of NO reduction increased linearly upon addition of ethylene.

Synthesis of Highly Active Superacids of SO₄/ZrO₂ with Ir, Pt, Rh, Ru, Os, and Pd Substances for Reaction of Butane

M. HINO and K. ARATA, *Catal. Lett.*, 1995, 30, (1-4), 25-30

Highly acidic catalysts, which are more acidic than the SO₄/ZrO₂ superacid and have an acid strength H_a ≤ -16.04, were prepared by kneading Zr(OH)₄ with NH₄ sulphate together with chlorides of Ir, Pt, Rh, Ru, Os and Pd, followed by calcining in air at 600°C. The metal concentration was equivalent to that of Pt, of 7.5 wt.%, based on the hydroxide. The catalysts with Ir and Pt materials had the highest activity for the skeletal isomerisation of butane to isobutane.

Preparation of Bimetallic Pt-Au Catalysts by Redox Reaction: Characterisation by XRD and SAXS

V. BERTIN, P. BOSCH, G. DEL ANGEL, R. GOMEZ, J. BARBIER and P. MARÉCOT, *J. Chim. Phys., Phys.-Chim. Biol.*, 1995, 92, (1), 120-133

Bimetallic Pt-Au/SiO₂ catalysts were prepared by surface redox reactions by introducing Au as AuCl₄⁻ reduced on the Pt surface either by H₂ preadsorbed or by direct oxidation of Pt⁰ by AuCl₄⁻. Spectroscopic studies showed that the bimetallic aggregates are formed from Au particles deposited on Pt particles, with reciprocal diffusion between the two metals.

Catalytic Synthesis of Unsaturated Nitriles from NO-Alkane or NO-Alkene on Pt-Sn/SiO₂

T. INOUE, K. TOMISHIGE and Y. IWASAWA, *J. Chem. Soc., Chem. Commun.*, 1995, (3), 329-330

Unsaturated nitriles were produced on Pt-Sn/SiO₂ catalysts, prepared by the selective bimetallic CVD reaction of SnMe₄ with Pt particles on SiO₂. The yields of acrylonitrile obtained from NO + propene and methacrylonitrile from NO + isobutene and NO + isobutane, had selectivities of ~70-93%, when compared with little activity and selectivity with unmodified Pt/SiO₂. Both the rate and selectivity of acrylonitrile formation increased with Sn content and reached a maxima at Sn:Pt = 0.2. NO dissociation and allyl hydrogen abstraction are thus promoted on Pt-Sn bimetallic ensemble sites.

Synthesis of Hydroxamic Acids: Pd/BaSO₄ as a New Catalyst for the Deprotection of O-Benzyl Hydroxamates

S. S. NIKAM, B. E. KORNBERG, D. R. JOHNSON and A. M. DOHERTY, *Tetrahedron Lett.*, 1995, 36, (2), 197-200

5% Pd/BaSO₄ was found to be an efficient catalyst in the deprotection of O-benzyl hydroxamates, dissolved in MeOH, by hydrogenation to give the corresponding hydroxamic acids without further reduction to amides. The reaction mixture was filtered and the filtrate evaporated to give the desired product in good to excellent yields after purification. Various hydroxamic acids were synthesised.

Hydrogen Storage by the Bicarbonate/Formate Reaction. Studies on the Activity of Pd Catalysts

H. KRAMER, M. LEVY and A. WARSHAWSKY, *Int. J. Hydrogen Energy*, 1995, 20, (3), 229-233

Studies of storage and generation of H₂ within the bicarbonate/formate reaction, showed that the Pd catalyst used loses its activity with time, but can be regenerated by air oxidation. CO poisoned the catalyst in both the forward and the back reactions. The Pd catalysts, based on polymer stabilised microdispersions, prepared from Na₂PdCl₄ and NaH₂PO₄, were active as the C-supported catalysts for H₂ generation. H₂ could be generated at pressures as high as 20 atm.

The Effect of Alumina Phase Structure on the Dispersion of Rhodium/Alumina Catalysts

R. W. MCCABE, R. K. USMEN, K. OBER and H. S. GANDHI, *J. Catal.*, 1995, 151, (2), 385-393

Rh was impregnated onto δ, θ and α Al₂O₃ at a loading of 0.6 μmol Rh/m² and the resultant Rh/Al₂O₃ catalysts were hydrothermally aged by treating in 10% H₂O/air at 1223 K for 24 h. TPR and other measurements identified 3 broad Rh forms: occluded, strongly interacted and non-interacted. A pronounced loading effect was observed for the α-Al₂O₃. The combined effects of an α-Al₂O₃ support, steam/air high temperature ageing prior to Rh deposition at < 1 μmol/m², maximised Rh dispersion and produced a more active catalyst than Rh deposited on higher surface area transitional Al₂O₃.

Rh-Loaded CeO₂-ZrO₂ Solid Solutions as Highly Efficient Oxygen Exchangers: Dependence of the Reduction Behavior and the Oxygen Storage Capacity on the Structural Properties

P. FORNASIERO, R. DI MONTE, G. RANGA RAO, J. KASPAR, S. MERIANI, A. TROVARELLI and M. GRAZIANI, *J. Catal.*, 1995, 151, (1), 168-177

Monoclinic, tetragonal and cubic structures of the binary Rh-loaded CeO₂-ZrO₂ systems were reported during TPR in a H₂/Ar mixture with 10-90% ZrO₂. Incorporation of ZrO₂ into a solid solution with CeO₂ strongly promotes bulk reduction of the Rh-loaded solid solutions compared with Rh/CeO₂. This structural dependence is attributed to a higher O mobility in the cubic structure compared to the tetragonal and monoclinic ones.

HOMOGENEOUS CATALYSIS

Palladium- and Platinum-Catalyzed Coupling Reactions of Allyloxy Aromatics with Hydrosilanes and Hydrosiloxanes: Novel Liquid Crystalline/Organosilane Materials

A. SELLINGER, R. M. LAINE, V. CHU and C. VINEY, *J. Polymer Sci. A, Polymer Chem.*, 1994, **32**, (16), 3069–3089

Pt- and Pd-catalysed reactions of allyloxyaromatic mono- and diesters with selected silanes were studied to develop simple methods of forming liquid crystal (LC)/siloxane and LC/silsesquioxane polymers. Pt complexes catalysed hydrosilylation to give primarily ($\leq 80\%$ selectivity at 100% conversion) terminal silylation of the allyloxys, with Pt-1,3-divinyltetramethyldisiloxane giving the cleanest reactions under the mildest conditions. Ph₃P[Pd(dba)₂/Ph₃P] gave the cleanest oxy-silylation reactions.

Palladium Catalysed Allylic Substitution Reactions of Prochiral and Racemic Allyl Acetates

G. J. DAWSON, J. M. J. WILLIAMS and S. J. COOTE, *Tetrahedron. Lett.*, 1995, **36**, (3), 461–462

The reaction of non-symmetrical allyl acetates and sodiodimethylmalonate catalysed by [Pd(allyl)Cl]₂ gave high yields and enantioselectivities of $\leq 99\%$ ee, using a diphenylphosphinoaryl oxazoline ligand (1). It is assumed that alternative π -allyl Pd complexes can interconvert by the π - σ - π mechanism. Thus substrates where the termini of Pd allyl intermediate are non-equivalent give enantioselective reactions with (1).

The Kinetics and Mechanism of Styrene Hydrocarboxylation Catalysed by PdCl₂(Ph₃P)₂ Complex. II. The Effect of the Styrene, Palladium Complex and Triphenylphosphine Concentration on the Rate and Regioselectivity of the Process

YU. G. NOSKOV and E. S. PETROV, *Kinet. Katal.*, 1994, **35**, (5), 728–733

The effect of a catalytic system containing styrene PdCl₂(Ph₃P)₂ and Ph₃P, on the initial rate of formation of hydrocarboxylation products 3- and 2-phenylpropionic acid, (1) and (2), respectively, was studied. The rates of formation of both compounds were linear depending on the concentrations. The formation of (2) increased with styrene concentration, but with increasing Ph₃P, concentration the formation of (2) greatly decreased; H₂O enhanced the decrease.

Synthesis of Allylsilanes by Palladium(0) Catalyzed Reduction of Trialkylsilylallyl Esters

J. OLLIVIER and J. SALAÜN, *Synlett*, 1994, (11), 949–951 Pd(0) catalysed reduction of trialkylsilylallyl esters by hydrides from HCOONa or *n*-BuZnCl (β -elimination) led to allylsilanes as major products, under mild conditions, suggesting a new and stereoselective route to electrophilic reagents. Pd(0) was Pd(OAc)₂:PPh₃ in ratio 1:2. When Pd is exclusively positioned on the ring then hydrided substitution occurred at the α or γ of the silyl group, depending on the hydride source.

Highly Selective Palladium Catalyzed Hydrogen Transfer from H₂O-CO to the C=C Double Bond of β -Benzoylacrylic Acid

G. CAVINATO, L. RONCHIN and L. TONIOLO, *J. Mol. Catal.*, 1994, **94**, (2), 173–180

A Pd-HCl catalytic system is very active and selective for H transfer from H₂O-CO to the olefinic double bond of the unsaturated γ -ketoacid PhCOCH=CHCOOH to PhCOCH₂CH₂COOH. High yields are obtained only when the Pd catalyst is used in combination with HCl. Pd/C also showed high activity. Addition of HCl to the olefinic double bond of the substrate gives PhCOCH₂CHClCOOH, which oxidatively adds to “reduced Pd” to form an intermediate with a Pd-[CH(COOH)CH₂COPh] moiety.

Palladium(0) Complex-Catalyzed Debrominative Coupling of (Tribromomethyl)- and (Dibromomethyl)benzenes to Diarylacetylenes and 1,2-Diarylethenes

S. MATAKA, G.-B. LIU and M. TASHIRO, *Synthesis*, 1995, (2), 133–135

Pd(0)-triphenylphosphine complex catalysed the debrominative coupling reaction of (tribromomethyl) benzenes to give diarylacetylenes or a mixture of (*E*)- and (*Z*)- α,β -dibromostilbenes, depending on the substrate and the solvent used. The coupling reaction was studied using three catalytic systems: Pd(PPh₃)₄; a combination of Pd(II) acetate, triphenyl phosphine and triethylamine; and Pd(PPh₃)₂Br and triethylamine. A great acceleration in the coupling reaction was observed in *N,N*-dimethylacetamide, compared with that in dimethylformamide.

Hydroformylation with a Rhodium/Bulky Phosphite Modified Catalyst. Catalyst Comparison for Oct-1-ene, Cyclohexene, and Styrene

A. VAN ROOY, E. N. ORIJ, P. C. J. KAMER and P. W. N. M. VAN LEEUWEN, *Organometallics*, 1995, **14**, (1), 34–43

Hydroformylation of oct-1-ene, cyclohexene and styrene was studied using Rh(CO)₂acac as the catalyst precursor and tris(2-*tert*-butyl-4-methylphenyl) phosphite (1) as the ligand at 40–100°C, under CO and H₂ pressures of 2.4–44 and 2.5–50 bars, respectively, in toluene as a solvent. Very high hydroformylation rates were obtained for oct-1-ene under mild conditions. The rate-determining step is the reaction of H₂ with the acyl Rh complex. The Rh catalyst combined with (1) is an excellent catalyst, particularly for unsubstituted alk-1-enes under mild conditions.

Rhodium-Catalyzed Modification of Poly-(methylhydrosiloxane) into a Highly Cross-Linked Polysiloxane

N. SATYANARAYANA and H. ALPER, *Macromolecules*, 1995, **28**, (1), 281–283

Modification of poly(methylhydrosiloxane) was achieved using a Rh complex catalyst, such as RhCl(PPh₃)₃ and [Rh(CO)₂Cl]₂ via a dehydrogenative coupling reaction followed by in-situ oxidation of the Si-Si bond under mild conditions. The reaction gave a thermally stable cross-linked polysiloxane.

New Hydroformylation Rhodium Catalysts with Dithiolate Chiral Ligands

A. M. MASDEU, A. OREJÓN, A. RUIZ, S. CASTILLÓN and C. CLAVER, *J. Mol. Catal.*, 1994, **94**, (2), 149–156
A new precursor system using Rh(I) complex catalyst with a bridge dithiolate chiral ligand: $[\text{Rh}_2(\mu\text{-}(-)\text{-DIOS})(\text{cod})_2]_n$, $n = 2$ (1) and $n = 1$ (2); (where $(-)\text{-DIOS}$ is 2,3-*O*-isopropylidene-1,4-dithio-L-threitol and cod: 1,5-cyclooctadiene), was used for asymmetric hydroformylation of styrene. System (1) gave high conversion to corresponding aldehydes (100% at 30 bar, 65°C) with a selectivity in 2-phenylpropanal of 64%. On addition of PPh_3 , selectivity was further increased to 91% under the same conditions.

Cis-[RhI(CO)(Ph₂PCH₂P(S)Ph₂): A New Catalyst for Methanol Carbonylation

M. J. BAKER, M. F. GILES, A. G. ORPEN, M. J. TAYLOR and R. J. WATT, *J. Chem. Soc., Chem. Commun.*, 1995, (2), 197–198

The complexes *cis*-[RhI(CO)(Ph₂PCH₂P(S)Ph₂)] was found to be 8 times more active than the classic Monsanto catalyst $[\text{RhI}_2(\text{CO})_2]$ for the carbonylation of methanol at 185°C. This catalytic system is the first promoted system effective under conditions which allow industrially realistic rates. An X-ray crystal structure study of the analogue complex *cis*-[RhCl(CO)-(Ph₂PCH₂P(S)Ph₂)] is reported.

Formation of 2-Alkylaminoxazoles by the Rh₂(OAc)₄-Catalyzed Reaction of α -Diazocarbonyl Compounds in the Presence of Cyanamides

K. FUKUSHIMA and T. IBATA, *Heterocycles*, 1995, **40**, (1), 149–154

The Rh₂(OAc)₄-catalysed reaction of α -diazoacetophenones with *N,N*-dialkylcyanamides (1) yielded the corresponding 2-(*N,N*-dialkylamino)-5-aryloxazoles in high yields and could be used as the general method for the synthesis of 2-alkylamino-5-aryloxazoles. Unsubstituted and monosubstituted cyanamides gave the corresponding 2-aminooxazoles in low yields. 2-(*N,N*-Dialkylamino-5-alkoxyoxazoles formed by the similar reaction of diazoacetates with (1) were found to be unstable upon isolation.

Rh₂(OAc)₄-Catalysed Cycloaddition of Ethyl Diazoacetate to 1,2-Dialkoxybenzenes: a New Type of Stable Norcaradiene

M. MATSUMOTO, T. SHIONO, H. MUTOH, M. AMANO and S. ARIMITSU, *J. Chem. Soc., Chem. Commun.*, 1995, (1), 101–102

Studies of Rh₂(OAc)₄-catalysed cycloaddition of ethyl diazoacetate to 1,2-methylenedioxybenzene yielded the corresponding cycloheptatrienes, but the reaction of 1,2-dimethoxybenzene gave a new type of stable norcaradiene (1). Treatment of (1) with tetracyanoethylene in benzene at room temperature gave exclusively the Diels-Alder adduct. The transesterification of (1) with MeONa in MeOH caused ring-opening of the cyclopropane and the double bond isomerisation to afford cycloheptatrienes in 77% yield, but the hydrolysis of (1) by NaOH gave a complex mixture.

Asymmetric Catalytic Hydrogenation of α -Ketoesters Using New Chiral Ru(II)(AMPP) Complexes

F. HAPIOT, F. ASBOUSSOU and A. MORTREUX, *Tetrahedron: Asymmetry*, 1995, **6**, (1), 11–14

The reaction of the appropriate Ru precursor with amino(amido)phosphinephosphinite ligands produced the corresponding Ru-bismethylallyl complexes: Ru(AMPP)(CH₂C(CH₃)CH₂)₂ and biscarboxylate Ru(AMPP)(OCOR)₂ (R = CH₃ or CF₃) complexes. These complexes act as efficient catalyst precursors for the homogeneous asymmetric hydrogenation of α -ketoesters with enantiomeric excess up to 79%.

Asymmetric Hydrogenation of Olefins with Aprotic Oxygen Functionalities Catalyzed by BINAP-Ru(II) Complexes

T. OHTA, T. MIYAKE, N. SEIDO, H. KUMOBAYASHI and H. TAKAYA, *J. Org. Chem.*, 1995, **60**, (2), 357–363

Cyclic α,β -unsaturated ketones, alkylidene lactones and alkenyl ethers were hydrogenated in high enantiomeric excesses by BINAP-Ru(II) complexes (BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl) as catalysts. These 5-membered cyclic ketones, lactones and ethers having exocyclic C=C bonds were hydrogenated in very high enantioselectivities of ~98%. With alkenyl esters and ethers, ethereal O is important for the enantioface differentiation. The asymmetric hydrogenation can be successfully applied to the synthesis of (*R*)-4-methyl-2-oxetanone, which is a useful monomer for biodegradable polymers.

A Ru Catalyzed Addition of Alkenes to Alkynes

B. M. TROST, A. F. INDOLESE, T. J. J. MÜLLER and B. TREPTOW, *J. Am. Chem. Soc.*, 1995, **117**, (2), 615–623

Thermal bimolecular addition of unactivated alkenes to unactivated alkynes was performed using several Ru complexes including (PhOCH₃)(Ph₃P)RuCl₂, (*p*-cymene)(Ph₃P)RuCl₂, (*p*-cymene)[(C₆H₅)₃P]RuCl₂ and CpRu(COD)Cl. The latter Ru complex gave the highest conversions and regioselectivities in aqueous DMF at 100°C or MeOH at reflux. Internal and terminal alkynes react. The reaction has great chemoselectivity and control of product double bonds.

Structure and Mechanism in Aerobic Alkene Epoxidations Promoted by Ruthenium Complexes of Bis(dihydrooxazole) Ligands

S. BENNETT, S. M. BROWN, G. CONOLE, M. KESSLER, S. ROWLING, E. SINN and S. WOODWARD, *J. Chem. Soc., Dalton Trans.*, 1995, (3), 367–376

Reaction of $[\text{RuCl}_2(\text{NCMe})_2(\text{cod})]$ with bis(dihydrooxazoles) gave $[\text{RuCl}_2(\text{cod})\{(S,S)\text{-R}_2^1\text{C}(\text{C}=\text{NCHR}^2\text{CR}^1\text{O})_2\}]$ where cod = cycloocta-1,5-diene; R¹ = H, R² = CH₂Ph or Prⁱ; R¹ = Me, R² = Prⁱ. Mechanistic studies of the epoxidation of styrene and stilbenes in the presence of isobutyraldehyde and O₂ using the Ru complexes as catalysts were performed with and without 4-*tert*-butylcatechol as a radical trap. The metals acted as promoters for the production of PrⁱCO₂H which carried out the epoxidation either directly or by the formation of oxo-Ru species.

Ruthenium Tetroxide as a Phase Transfer Catalyst in Biphasic System and Its in situ Electrochemical Regeneration: Oxidation of Aromatic Primary Alcohol and Aldehydes

S. RAJENDRAN and D. C. TRIVEDI, *Synthesis*, 1995, (2), 153-154

RuO₄ was used as a phase transfer catalyst in a biphasic system of CCl₄ and saturated NaCl at a platinised Ti anode to regenerate spent oxidant for the oxidation of benzyl alcohol (1), benzaldehyde (2) and *p*-anisaldehyde (3). The pH of the system was almost neutral and therefore the oxidation was due to RuO₄ and not by RuO₃ and RuO₃²⁻. RuO₃ generated in the CCl₄ layer oxidised (1) to (2), (2) to benzoic acid and (3) to *p*-anisic acid in good yields.

Regiocontrolled Hydrosilation of α,β -Unsaturated Carbonyl Compounds Catalyzed by Hydridotetrakis(triphenylphosphine)-rhodium(I)

G. Z. ZHENG and T. H. CHAN, *Organometallics*, 1995, 14, (1), 70-79

The hydrosilation of α,β -unsaturated carbonyl compounds catalysed by (Ph₃P)₄RhH was found to be highly regioselective, depending on the silanes used. Diphenylsilane gave 1,2-hydrosilation, but dimethylphenylsilane and other monohydrosilanes gave 1,4-addition. The kinetic isotope effect of the hydrosilation reaction was examined. This catalyst gives milder reaction conditions than (Ph₃P)₃ClRh.

FUEL CELLS

Oxidation of Methane over Platinum in a Solid Proton-Conducting Electrolyte Cell

V. D. BELYAEV, V. V. GAL'VITA, V. P. GORELOV and V. A. SOBYANIN, *Catal. Lett.*, 1995, 30, (1-4), 151-158

The complete oxidation of CH₄ on a Pt electrode-catalyst in the cell with a solid proton-conducting electrolyte of (CH₄ + O₂, Pt / SrCe_{0.92}Dy_{0.08}O₃ / Pt, H₂O + N₂) was studied. The induced change in the reaction rate at anodic polarisation of a Pt electrode-catalyst was found to be more than two orders of magnitude higher than the rate of H pumping from the reaction zone through the electrolyte.

CHEMICAL TECHNOLOGY

Synthesis of Palladium Impregnated Alumina Membrane for Hydrogen Separation

S.-J. LEE, S.-M. YANG and S. B. PARK, *J. Membrane Sci.*, 1994, 96, (3), 223-232

A Pd impregnated Al₂O₃ membrane was prepared directly by mixing Al₂O₃ sol with a Pd precursor, followed by sonication to disperse the Pd particles uniformly throughout the membrane. A H-selective γ -Al₂O₃ membrane containing Pd particles was formed as an intermediate layer in an asymmetric porous support. The average pore radius and surface area measured by BET were 20.8 Å and 217.4 m²/g, respectively. The dispersion of Pd in the membrane is 0.31 and the particle size is 32 Å.

ELECTRICAL AND ELECTRONIC ENGINEERING

Magneto-Optic and Optical Properties of Multilayered Co/Pd Films

YU. V. KUDRYAVTSEV and R. GONTAZH, *Fiz. Met. Metalov.*, 1994, 77, (6), 44-52

Magneto-optic and optical properties of multilayered Co/Pd films in various stages of modulated composition were studied at 293 K over a wide spectral region. Results showed that the value of the magneto-optic effect in a monolayer Co/Pd film 1 μ m thick was proportional to the volume of Co concentration in the layer. Variations of this dependence occurred in the UV spectral region with decrease in the layer thickness, due to polarisation of the Pd layer position at a small distance from the Co layer and to the changes in magneto-optic parameters in very thin Co layers.

Hydrogen-Sensitive Property of Switching Device with a Pd-Si Tunnel Insulator Semiconductor Structure

S. NAKAGOMI and T. YAMAMOTO, *Jpn. J. Appl. Phys.*, 1994, 33, (11), 6136-6140

The effect of atmosphere on a switching device with a Pd-Si tunnel metal insulator semiconductor (MIS) structure was studied. The MIS device, Pd-insulator-(*n*)Si-(*p*')Si structure, showed negative-resistance switching properties. Work function data were obtained. O₂ increased the work function of Pd while H₂ decreased it.

A Comparison Study of Pd/In/Pd, Pd-In/Pd, and Pd-In Ohmic Contacts to *n*-GaAs

H. G. FU and T. S. HUANG, *Solid-State Electron.*, 1995, 38, (1), 89-94

Metallurgical and electrical characteristics of layer-deposited (1) Pd/In/Pd and codeposited (2) Pd-In/Pd and Pd-In ohmic contacts to *n*-GaAs were studied. The codeposited contacts (2) have smooth surfaces, and their minimum specific contact resistances are 3×10^{-6} Ω cm² after annealing at 600°C for 10 s. However, contacts (1) have rough surfaces with many hollow blisters which are explained by the local vapourisation of In during deposition of the outermost Pd layer. The contact resistance of all (1) and (2) contacts increased with time after 400°C ageing.

TEMPERATURE MEASUREMENT

Design of RuO₂-Based Thermometers for the Millikelvin Temperature Range

I. BAT'KO, K. FLACHBART, M. SOMORA and D. VANICKY, *Cryogenics*, 1995, 35, (2), 105-108

Thick RuO₂-based thick film resistors were designed as low temperature thermometers in the millikelvin temperature range. These resistors can be used as an alternative to Ge ones, and both the R-T characteristics and the sensitivities can be altered simply by changing the distance between conduction pads. The temperature dependence of the resistance of RuO₂ sensors at the lowest temperatures studied is described in terms of a variable-range hopping mechanism.