

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Platinum Etching and Plasma Characteristics in RF Magnetron and Electron Cyclotron Resonance Plasmas

K. NISHIKAWA, Y. KUSUMI, T. OOMORI, M. HANAZAKI and K. NAMBA, *Jpn. J. Appl. Phys.*, 1993, 32, (12B), 6102–6108

Pt etching was examined using r.f. magnetron plasma (1) and electron cyclotron resonance (ECR) plasma at 0.4–50 Torr in Cl_2 plasmas. For (1) the etch rate of Pt was constant at substrate temperature 20–160°C. The etch rate and plasma electron density increased with decreasing gas pressure from 50 to 5 mTorr. In ECR plasma for r.f. power of 300 W, the etch rate of Pt was almost constant at ~100 nm/min at gas pressure of 5–0.4 Torr, while the plasma electron density was gradually increased with decreasing gas pressure. Highly accurate sub-micron patterning of 0.5 μm lines and spaces of Pt masked with photoresist was achieved using Cl_2 plasmas in ECR discharges.

Effect of Diamond Facet on the Electrical Properties of Pt/BF_2^+ Ion Implanted Polycrystalline Diamond Contacts

Y. T. CHENG, S. J. LIN and J. HWANG, *Appl. Phys. Lett.*, 1993, 63, (24), 3344–3346

The effect of the diamond facet on the electrical properties of Pt/polycrystalline diamond contacts grown on Si(100) substrates at different positions of the plasma ball in a microwave plasma enhanced CVD chamber was examined. The Pt/BF_2^+ ion implanted polycrystalline diamond contacts had different properties although the Raman spectra were almost the same. Pt/BF_2^+ ion implanted polycrystalline diamond contacts showed Schottky behaviour for diamond film with major facet (100) whereas Pt/BF_2^+ ion implanted polycrystalline diamond contacts exhibited ohmic behaviour for the diamond film with major facet (111).

Electrocrystallization of Cobalt/Platinum Multilayers

Y. JYOKO, S. KASHIWABARA and Y. HAYASHI, *Mater. Trans. JIM*, 1993, 34, (10), 946–951

Co electrocrystallisation on Pt(111) surfaces was examined in order to produce Co/Pt superlattices of comparable structure and magnetic properties to those prepared by vapour phase deposition. REM-RHEED studies carried out under potential control showed that simultaneous multinuclear multilayer growth up to 10 monolayer coverage could be obtained. Room temperature magnetic measurements were made on the electrodeposited $[\text{Co}(2 \text{ nm})/\text{Pt}(4 \text{ nm})]_{50}$ multilayers. Their magnetic properties tend to exhibit in-plane anisotropy, but remnant perpendicular magnetisation for the multilayer with a rougher interface electrodeposited under a higher overpotential.

Catalytic Role of Nickel, Palladium, and Platinum in the Formation of Carbon Nanoclusters

S. SERAPHIN, D. ZHOU, J. JIAO, M. A. MINKE, S. WANG, T. YADAV and J. C. WITHERS, *Chem. Phys. Lett.*, 1994, 217, (3), 191–198

Carbon clusters were prepared by arc discharge from graphite anodes containing Pt, Pd or Ni under nanotube production conditions. No nanotubes and very few nanoparticles were found to be encapsulated. With Pt in the anode the highest density of nanotubes was formed in the cathode deposit, while Pd-filled anodes produced the lowest density of nanotubes. The Pt-produced cathode deposit has columnar structure, while the Pd-produced cathode deposit is like molten clay, of laminar structure, having lower nanotube density.

TEM and AES Characterization of Thin Films of Au, Pt and Pd Deposited on Mica

R. PEREZ, L. FIONOVA and L. MORALES DE LA GARZA, *Mater. Lett.*, 1994, 18, (4), 223–228

Highly pure Pt, Pd and Au were thermally evaporated as ~200 nm films of f.c.c. structure on mica under high vacuum conditions. Layer by layer AES showed contamination of the film surfaces with S and preferentially with C decreasing inside the film with distance from the surface. Oxygen in the film tends to diffuse into the Pd especially at the metal/mica region. At the Pt/mica and Au/mica interfaces are K and traces of Si, respectively. The films are polycrystalline with preferential <111> orientation.

Magnetic Properties of ErPt_2Si_2

J. P. SANCHEZ, A. BLAISE, K. TOMALA and R. KMIEC, *Solid State Commun.*, 1994, 89, (7), 647–649

Susceptibility measurements and magnetisation measurements were carried out on ErPt_2Si_2 at 1.5–300 K using a SHE-SQUID magnetometer or an Oxford Faraday balance, giving magnetic fields up to 50 kOe. The compound crystallises with the CaBe_2Ge_2 type structure, and remains paramagnetic down to 1.5 K. It is concluded that the Er moment associated with the ground state amounts to $8.25(20)\mu_B$ which is very close to the full moment of $9\mu_B$ for Er^{3+} ions.

Carbon Monoxide Adsorption on a $\text{Pt}_{80}\text{Fe}_{20}(111)$ Single-Crystal Alloy

A. ATLI, M. ABON, P. BECCAT, J. C. BERTOLINI and B. TARDY, *Surf. Sci.*, 1994, 302, (1/2), 121–125

HREELS measurements of CO adsorption on the $\text{Pt}_{80}\text{Fe}_{20}(111)$ single crystal alloy at 120 K showed that CO was adsorbed mainly on the top layer although bridge-bonded CO also occurred near saturation. CO adsorption on Pt-rich surface of $\text{Pt}_{80}\text{Fe}_{20}(111)$ exhibits significant differences compared to CO on Pt(111). The presence of Fe atoms in the sub-surface induces the observed decrease in the CO binding energy.

Solid State Reactions between Pd and Si Induced by High Energy Ball Milling

D. L. ZHANG and T. B. MASSALSKI, *J. Mater. Res.*, 1994, 9, (1), 53–60

The phases resulting from diffusion during high energy ball milling between Pd and Si depend on the amount of Si present. At 19 % Si, an amorphous phase forms and becomes Pd₂Si₃ and Pd₂Si on continued milling. At Si contents ≥ 33 at. %, Pd₂Si phase was produced but no amorphous phases. For powder compositions corresponding to the stoichiometric compound Pd₂Si at 33 at. % Si, Pd₂Si forms and remains stable during further milling. At Si contents of ≥ 50 at. % the Pd₂Si is destabilised by a reaction with Si to form PdSi, which is metastable at the temperature of ball milling.

Reliability and Microstructure of Al-Si-V-Pd Alloy Films for Use in Ultralarge Scale Integration

A. G. DIRKS and R. A. AUGUR, *Appl. Phys. Lett.*, 1994, 64, (6), 704–706

Highly reliable Al-based quaternary Al-Si-V-Pd films were studied and compared to conventional ternary Al-Si-Cu alloy films. The Al-Si-V-Pd films containing 0.1 at. % V and 0.1 at. % Pd displayed excellent plasma etchability together with good corrosion resistance. Electromigration tests of Al-Si-V-Pd films showed a high stability at 180°C. Highly stable microstructure is due to the presence of finely dispersed, small precipitates of both (Al,V) and (Al,Pd) phases.

Plastic Deformation in Icosahedral Al-Pd-Mn Alloys

J. E. SHIELD, M. J. KRAMER and R. W. MCCALLUM, *J. Mater. Res.*, 1994, 9, (2), 343–347

Deformation in the face-centred icosahedral phase in Al-Pd-Mn alloys at high temperatures and 23.6–47.3 MPa was investigated by TEM after preparation from the high purity metals of nominal composition Al₇₀Pd_{21.5}Mn_{8.5}. At 730–780°C, deformation was controlled by dislocation glide with activation energy of 210 ± 30 kJ/mole and stress exponent of 1.2 ± 0.2 . At 780–810°C, microstructures were characteristic of deformation controlled by dislocation glide and climb, with activation energy of 1700 ± 80 kJ/mole and stress exponent 2.9 ± 0.3 . Deformed samples were ~ 10 % harder than as-cast samples.

Dislocation-Enhanced Hydrogen Solubilities in Pd-Ni, Pd-Ag and Pd-Ni-Ag Alloys

S. KISHIMOTO, N. YOSHIDA, T. HIRATSUKA, A. NAKANO, T. MASUI and T. B. FLANAGAN, *Scr. Metall. Mater.*, 1994, 30, (5), 643–647

The solubility enhancements for cold-worked Pd-Ni alloys were determined for a series of homogeneous ternary Pd_{1-x}Ni_{0.5x}Ag_{0.5x} with $x = 0-0.2$ at 273–348 K. Substitutional Ag in Pd increases the lattice size, but substitutional Ni decreases the Pd lattice. Pd-Ni forms a series of f.c.c. solid solution alloys over the entire composition range. A mechanism is suggested where the larger Ag and the smaller Ni substitutional solute atoms segregate to or leave the tensile stress fields, respectively, during cold working of the binary alloys.

Structural Phase Transformation and Shape Memory Effect in ZrRh and ZrIr

E. L. SEMENOVA and YU. V. KUDRYAVTSEV, *J. Alloys Compd.*, 1994, 203, 165–168

Crystal structure investigations of ZrRh and ZrIr compounds have shown a B19'-type phase at room temperatures, a B2-type phase at 670 and 1050°C, respectively and a b.c.c. phase for ZrRh in the temperature range 1455°C to melting point. For a ZrRh specimen of $0.8 \times 2 \times 20$ mm³ in size at a load of 400 gf, a shape memory effect caused by the structural transformation on cooling of B2 \leftrightarrow B19' with a transformation hysteresis width of ~ 200 °C was found. Full shape restoration took place after > 20 heating/cooling cycles. A similar shape memory effect is expected for ZrIr.

Fracture Behaviour of Polycrystalline Iridium under Tension in the Temperature Range 20–1500°C

P. PANFILOV, V. NOVGORODOV and A. YERMAKOV, *J. Mater. Sci. Lett.*, 1994, 13, (2), 137–141

The fracture behaviour under tension of dangerous-impurity-free polycrystalline Ir and alloy Ir-0.3 wt. % Re-2 wt. % Ru was studied at 20–1500°C. The wire specimens were made from a single crystal rod without any annealing and stretched at 1 mm/min for 15 min. The fracture mode of the single crystals and polycrystalline Ir, both C-free, was brittle transgranular (BTF), in the latter BTF was seen in the neck region after plastic deformation. Transition from BTF to brittle intercrystalline fracture (BIF) in the alloy at temperatures > 1250 °C may be connected to C and other contaminants. BIF is environmentally induced fracture without prior specimen deformation.

High-Temperature Stability of Heteroepitaxial Ir-Silicide/SiGe Layers Co-deposited on Si(100) under Ultra-High Vacuum

C. K. CHUNG and J. HWANG, *Thin Solid Films*, 1994, 239, (1), 112–116

Heteroepitaxial Ir-silicide/SiGe layers were grown on top of *p*-Si(100) at a substrate temperature of 450°C under UHV. A critical transition temperature existed at 550–750°C; epitaxial Ir₃Si₄/SiGe layers were stable when annealed at 550°C, but unstable during rapid thermal annealing at ≥ 750 °C for 20 s. The Ir₃Si₄ layer became a mixture of dual Ir-silicide phases containing Ge atoms as the instability occurred.

Grain Boundary Scattering in Ruthenium Dioxide Thin Films

S. Y. MAR, J. S. LIANG, C. Y. SUN and Y. S. HUANG, *Thin Solid Films*, 1994, 238, (1), 158–162

Studies of RuO₂ thin films with an average grain size of 12–50 nm deposited by reactive sputtering showed that the factors correlated to the resistivity of the films also govern the average grain size of the films. The grain boundary reflection coefficient for electrons in RuO₂ was 0.785. The total resistivity of RuO₂ polycrystalline films was affected by electron scattering due to the grain boundary. The resistivity of RuO₂ thin films could be 10 times higher than that of the bulk material and still have metallic behaviour.

Surface Structure of Semiconducting Ruthenium Pyrite (RuS₂) Investigated by LEED and STM

H. COLELL, M. BRONOLD, S. FIECHTER and H. TRIBUTSCH, *Surf. Sci. Lett.*, 1994, 303, (1/2), L361-L366

Atomic resolution scanning tunnelling microscopy images of (100) cleavage planes of semiconducting RuS₂ are presented. RuS₂ has a remarkable stability against reactions under ambient conditions and its surface appears to be essentially unreconstructed. This may be due to the pronounced low energy of electronic surface states of pyrite-type compounds which is known for FeS₂.

CHEMICAL COMPOUNDS

Giant Pd Clusters Observed by High Resolution Electron Microscopy

V. V. VOLKOV, G. VAN TENDELOO, M. N. VARGAFIK, I. P. STOLYAROV and I. I. MOISEEV, *Mendeleev Commun.*, 1993, (6), 187-188

Giant cationic Pd clusters of approximate formula Pd₅₆₁L₆₀(OAc)₁₈₀, where L is Diph or Phen, obtained by reduction from Pd(OAc)₂ with H₂ in acetic acid containing small amounts of Diph or Phen, followed by O₂ treatment, were characterised by TEM and electron diffraction. The metal core was f.c.c. and most Pd particles ≥ 8 exhibited multiple twinning, which is evidence for a distorted icosahedral structure.

Synthesis, Structure and Properties of CpRu(PPh₃)_nS₂P(OR)₂

S.-O. WU, Z.-G. LIU, Y.-L. ZHANG and P.-G. LI, *Gazz. Chim. Ital.*, 1993, 123, (11), 647-650

New derivatives of Ru with general formula CpRu(PPh₃)_nS₂P(OR)₂ (n = 1 or 2) were produced by reaction of CpRu(PPh₃)₂Cl (Cp = η⁵-C₅H₅, η⁵-MeC₅H₄) with (RO)₂PS₂M (M = Na, K, HNET₃; R = Me, CH₃, Et-, Ph-, p-MeC₆H₄-, α-naphthyl, o-phenylene) in MeOH. The compounds were characterised by NMR, IR spectra and chemical analysis.

ELECTROCHEMISTRY

Electroreduction of Molecular Oxygen on Preferentially Oriented Platinum Electrodes in Acid Solution

C. F. ZINOLA, A. M. CASTRO LUNA, W. E. TRIACA and A. J. ARVIA, *J. Appl. Electrochem.*, 1994, 24, (2), 119-125

The O electroreduction was studied on preferentially oriented Pt (111)-type (1) and (100)-type (2) electrodes, and on a conventional polycrystalline (PC) Pt rotating disc electrode in 1.0 M H₂SO₄ acid + K₂SO₄ solution at 30°C. At low overpotentials Tafel slopes of -0.060 V/decade were obtained for all three electrodes; at high overpotentials in 1.0 M H₂SO₄, the usual Tafel slope of -0.12 V/decade was observed for (1) and (PC), but -0.165 V/decade on (2). Surface coverage by O-containing adsorbates was greatest on (2), producing more H₂O₂. Surface blockage by SO₄²⁻ and HSO₄⁻ occurs on (111)-type Pt, while peroxide species are responsible for the (100)-type Pt blockage.

Comparison of Lead Zirconate Titanate Thin Films on Ruthenium Oxide and Platinum Electrodes

L. A. BURSILL, I. A. REANEY, D. P. VIJAY and S. B. DESU, *J. Appl. Phys.*, 1994, 75, (3), 1521-1525

The interfaces and microstructures in two PZT/RuO₂/SiO₂/Si and PZT/Pt/Ti/SiO₂/Si (1) ferroelectric thin films were examined by HRTEM to compare the improved fatigue characteristics of PZT thin films with RuO₂ electrodes. A nanocrystalline pyro-chlore phase Pb₂ZrTiO_{7-x}, where x ≠ 1 was found on the top surface of the PZT layer. Thin film (1) was well crystallised with sharp interfaces throughout.

CO Electrooxidation on Well-Characterized Pt-Ru Alloys

H. A. GASTEIGER, N. MARKOVIC, P. N. ROSS and E. J. CAIRNS, *J. Phys. Chem.*, 1994, 98, (2), 617-625

The electrocatalytic activity of Pt-Ru alloy electrodes for CO electrooxidation in acidic electrolyte at room temperature was measured on UHV-prepared alloy surfaces. CO stripping voltammetry and the potentiostatic oxidation of adsorbed CO showed maximum activity in alloys of surface composition ~ 50 at.% Ru, which corresponds to a surface with a maximum number of Pt-Ru pairs. Sputter-cleaned Pt-Ru alloy electrodes showed synergistic properties not observed in annealed Pt-Ru electrodes. This is attributed to a uniquely active state of OH_{ad} on Pt-Ru pair sites. The different electrode electrocatalytic activities are explained by Ru clustering during annealing, creating Ru nano-electrodes embedded in a Pt electrode.

UHV and Electrochemical Studies of the Surface Properties of Ru + Pt + Ti Mixed Oxide Electrodes

T. A. F. LASSALI, J. F. C. BOODTS, S. C. DE CASTRO, R. LANDERS and S. TRASATTI, *Electrochim. Acta*, 1994, 39, (1), 95-102

The behaviour of surface properties of Ru_{0.3}Pt_{0.7}Ti_{0.3}O₂, Ru_{0.3}Ti_{0.7}O₂ (DSA) and Pt_{0.4}Ti_{0.6}O₂ electrodes has been compared electrochemically and by UHV (oxides containing Pt have variable stoichiometry). Adding Pt to RuO₂ + TiO₂ electrodes changes their morphology with an increase in charge. Ru and Ti are in the +4 oxidation state, and Pt is in the +2 oxidation state. The high oxidation state of Pt may be linked to decomposition occurring in aqueous solution, and tends to decrease with potential cycling. The surface concentration of Pt in freshly prepared mixed oxides is higher than the nominal one.

Lignin Augmented Hydrogen Absorption by Palladium Cathode

S. MURALIDHARAN, M. ANBU KULANDAINATHAN and V. KAPALI, *Int. J. Hydrogen Energy*, 1994, 19, (3), 219-222

Cyclic voltammetry and H permeation studies carried out at the Pd/0.1 M NaOH interface showed that lignin enhances H adsorption on Pd during the cathodic polarisation. The kinetics of the cathodic reaction is controlled by H adsorption on the electrode surface for the Pd/NaOH interface but by mass transfer control for the Pt/NaOH interface.

Reproducible Tritium Generation in Electrochemical Cells Employing Palladium Cathodes with High Deuterium Loading

F. G. WILL, K. CEDZYNSKA and D. C. LINTON, *J. Electroanal. Chem.*, 1993, **360**, (1–2), 161–176

Reproducible T generation has been observed in tightly closed D₂SO₄ containing cells in four Pd wire cathodes. No T generation was observed in four identical Pd cathodes in H₂SO₄ cells under the same conditions. A cyclic loading/unloading regime used with low current density showed that D:Pd loadings of $> 0.8 \pm 0.05$ are needed to generate T. The most T generated in 7 days of continuous electrolysis was 2.1×10^{11} T atoms, compared with a background of 4×10^6 T atoms.

Electrochemical Hydrogen Discharge Characteristics of Pd and Pd-Ni-Rh Alloy Hydride Electrodes Catalysed by Pd/Pt-Black Coatings

Y. SAKAMOTO, K. KURUMA and Y. NARITOMI, *J. Appl. Electrochem.*, 1994, **24**, (1), 38–43

The electrochemical H discharge characteristics of pure Pd and Pd-Ni-Rh alloy hydride electrode, activated by a superimposed electrodeposited film of Pd/Pt-black, were studied as the negative electrode for Ni oxide-metal hydride battery. The best discharge characteristics were obtained for Pd-7.5 at.% Rh and/or Pd-2.5 at.% Ni-7.5 at.% Rh alloy hydride. The electrode surfaces were first activated with $\sim 1\text{--}2$ mg/cm² of Pd black and then with Pt black.

Electrochemical Copolymerization of Aniline and para-Phenylenediamine on IrO₂-Coated Titanium Electrode

C.-H. YANG and T.-C. WEN, *J. Appl. Electrochem.*, 1994, **24**, (2), 166–178

Cyclic voltammetry studies of the copolymerisation of aniline and *p*-phenylenediamine (1) on IrO₂-coated Ti electrodes in 0.5M H₂SO₄ showed a peak at about 580 mV corresponding to the *p*-aminophenol/benzoquinoneimine redox couple and cross-linking sites. The mass of polymer deposited on the IrO₂-coated Ti electrode is correlated with the polymer anodic peak current at various concentrations of (1). The morphology of the polymer film depends greatly on concentration of (1).

In-situ Twin-Electrode Spectroscopic Voltammetry with a Cell Composed of a Pair of Nafion-Coated Indium Tin Oxide Electrodes each Incorporating Ru(bpy)₃²⁺ and Methylviologen

T. ONIKUBO, R.-J. LIN and M. KANEKO, *J. Electroanal. Chem.*, 1993, **361**, (1–2), 143–148

Electrochemical redox reactions in a cell composed of two Nafion-coated indium tin oxide (ITO) electrodes were analysed. The cell system ITO/Nafion-[Ru(bpy)₃²⁺]/aqueous electrolyte/Nafion [MV²⁺]/ITO showed changes in the visible absorption spectra induced by cyclic scanning of the potential difference between the two ITO electrodes. The spectral changes were attributed to the redox reaction of the Ru and MV, showing multicolour electrochromism.

Thermoanalytical Investigation of the Formation of RuO₂-Based Mixed-Oxide Electrodes

J. KRISTÓF, J. LISZI, A. DE BATTISTI, A. BARBIERI and P. SZABÓ, *Mater. Chem. Phys.*, 1994, **37**, (1), 23–28

Formation of RuO₂/TiO₂ film coatings from precursor salts dissolved in isopropanol was studied. For pyrolysis of Ru and Ti salt mixtures, the final decomposition temperature was reduced by $> 100^\circ\text{C}$ due to the catalytic effect of the Ru addition. The highest rate of decomposition and heat release, and the maximum charge-storage capacity were observed for a coating composition of 10–30 mol% of Ru.

PHOTOCONVERSION

XPS-Characterization of Hydrogen-Evolving Platinum-Coated *p*-Silicon Photoelectrodes

G. BILGER, M. SPECHT, C. U. MAIER, A. EICKE and M. GILLMANN, *Appl. Surf. Sci.*, 1994, **75**, 157–163

The photoelectrochemical behaviour of homogeneous Pt films and microscopic Pt islands on top of *p*-doped Si were studied on Pt samples deposited on monocrystalline Si by physical vapour deposition and a photo-assisted electrochemical technique. Crystalline *p*-Si covered with Pt layers on the atomic scale operate as stable H-evolving photocathode. Only ultra-thin Pt submonolayers or microscopic islands can affect the H evolution at the photocathodes during long-term operation in various electrolytes.

Laser Flash Photolysis and Pulse Radiolysis Studies of Ruthenium Complexes

B. J. PARSONS, P. C. BEAUMONT, S. NAVARATNAM, W. D. HARRISON, T. S. AKASHEH and M. OTHMAN, *Inorg. Chem.*, 1994, **33**, (1), 157–163

Laser flash photolysis and pulse radiolysis techniques were used to obtain the absorption spectra of charge-transfer excited states and one-electron-reduced states of a number of mono- and binuclear Ru complexes in H₂O. Bimolecular rate constants for the reaction of e_{aq}⁻ with the above complexes and with the mixed-ligand complexes Ru(bpy)₂dpp²⁺ and Ru(bpy)₂dhp²⁺ were also determined.

ELECTRODEPOSITION AND SURFACE COATINGS

Covalent Binding of Pd Catalysts to Ligating Self-Assembled Monolayer Films for Selective Electroless Metal Deposition

W. J. DRESSICK, C. S. DULCEY, J. H. GEORGER, G. S. CALABRESE and J. M. CALVERT, *J. Electrochem. Soc.*, 1994, **141**, (1), 210–220

Selective electroless (EL) metallisation of surfaces is described; surfaces are modified with a ligand-bearing organosilane film then catalysed with chloride-containing Pd(II) solutions buffered at pH 5.0–6.4. Oligomeric chloro and/or hydroxo-bridged Pd(II) complexes act as the catalytic species at the surface. A minimum surface concentration of $\sim 10^{15}$ Pd atom/cm² is needed to start EL metallisation of a substrate.

Reductive Deposition of Pd on Porous Silicon from Aqueous Solutions of PdCl₂: An X-ray Absorption Fine Structure Study

I. COULTHARD, D.-T. JIANG, J. W. LORIMER, T. K. SHAM and X.-H. FENG, *Langmuir*, 1993, 9, (12), 3441-3445
Pd was successfully deposited on the large surface of porous Si from aqueous solutions of PdCl₂. The reductive deposition of Pd metal from PdCl₂(aq) occurred at specific surface sites by an oxidation-reduction reaction. Thus porous Si deposits Pd reductively on its surface from Pd(II) ions and so could be a suitable substrate for the deposition of noble metal and bimetallic catalysts.

Chemical Vapor Deposition of Ruthenium and Osmium Thin Films Using (Hexafluoro-2-butyne)tetracarbonylruthenium and -Osmium

Y. SENZAKI, W. L. GLADFELTER and F. B. MCCORMICK, *Chem. Mater.*, 1993, 5, (12), 1715-1721
Reflective pure polycrystalline Ru thin films can be produced by CVD from Ru(hfb)(CO)₄, where hfb is hexafluoro-2-butyne, by H₂ carrier gas, with a growth rate of 21 nm/min at 500°C. The resistivity of the film is 22 μΩ cm for a grain size of 60 nm. Polycrystalline thin Os films can be produced from Os(hfb)(CO)₄, using H₂ carrier gas, at a growth rate of 14 nm/min, resistivity of 81 μΩ cm, and grain size of 20 nm. The film consists of 84 % Os, 7 % O and 9 % C.

APPARATUS AND TECHNIQUE

Iridium-Based Ultramicroelectrode Array Fabricated by Microlithography

S. P. KOUNAVES, W. DENG, P. R. HALLOCK, G. T. A. KOVACS and C. W. STORMENT, *Anal. Chem.*, 1994, 66, (3), 418-423
The microlithographic fabrication of an Ir-based Hg ultramicroelectrode (UME) is described. The Hg was stable on the Ir without degradation or dissolution of the Ir pads after several days of use. The array has 19 interconnected 10 μm diameter UMEs and multiplies the signal current in proportion to the number of UMEs in the array, without overlap of the diffusion fields. The Hg UME can analyse Cd(II), Pb(II) and Cu(II) in spring water.

Luminescent pH Sensors Based on *p*-tert-Butylcalix[4]arene-Linked Ruthenium(II) Trisbipyridyl Complexes

R. GRIGG, J. M. HOLMES, S. K. JONES and W. D. J. AMILAPRASADH NORBERT, *J. Chem. Soc., Chem. Commun.*, 1994, (2), 185-187
A luminescent pH sensor based on *p*-tert-butylcalix[4]arene-linked trisbipyridyl Ru(II) complexes has been developed. The trisbipyridyl Ru(II) moiety (the luminophore) and the free phenolic units of the calix[4]arene acting as the acid-base sites, were coupled by a methylene spacer to maximise the electron transfer rate and to buffer the units. Photo-induced intramolecular electron transfer was caused by the formation of phenolate anions, thus quenching the luminescence. The sensor works in 50% aqueous MeOH by this photoinduced electron transfer.

HETEROGENEOUS CATALYSIS

From CH₄ Reforming with CO₂ to Pyrolysis over a Platinum Catalyst

Z. YU, K. CHOI, M. P. ROSYNEK and J. H. LUNSFORD, *React. Kinet. Catal. Lett.*, 1993, 51, (1), 143-149
At temperatures up to 1100°C CH₄ and CO₂ react over a Pt wire to give CO, even at a CH₄:CO₂ ratio of 4.3. But if coke is on the wire the dominant reaction becomes the pyrolysis of CH₄ to give mainly acetylene and benzene. Higher temperatures and larger CH₄:O₂ ratios favour the formation of coke and the pyrolysis. The O₂ and H₂O have the opposite effect.

Structure Characterization of Platinum/Alumina, Rhenium/Alumina, and Platinum-Rhenium/Alumina Catalysts

L. CHEN, Y. NI, J. ZHANG, L. LIN, X. LUO and S. CHENG, *J. Catal.*, 1994, 145, (1), 132-140
The structures of Pt/Al₂O₃, Re/Al₂O₃ and Pt-Re/Al₂O₃ catalysts were studied during the impregnation, calcination and reduction stages of preparation. Both Pt and Re reacted strongly with the support after calcination. The Pt species reacted more strongly with TiO₂ than with Al₂O₃. Pt(0), Re(0) and Pt₂Ti coexist in the reduced Pt-Re/Al₂O₃ catalyst. H adsorption at a high temperature increased with increasing Re:Pt ratio.

Preparation, Activity and Durability of Promoted Platinum Catalysts for Automotive Exhaust Control

J. R. GONZÁLEZ-VELASCO, J. ENTRENA, J. A. GONZÁLEZ-MARCOS, J. I. GUTIÉRREZ-ORTIZ and M. A. GUTIÉRREZ-ORTIZ, *Appl. Catal. B: Environ.*, 1994, 3, (2-3), 191-204
The effects of the additions of CaO, CeO₂ and La₂O₃ to Al₂O₃ supported Pt catalysts on the simultaneous control of HC, CO and NO_x automobile emissions were analysed. The activity of the samples was determined with steady-state, reducing and oxidising, simulated feedstreams, etc. The catalysts had better resistance to accelerated ageing, with catalysts modified with CeO₂ being the best. The catalysts had lower light-off temperatures than the known Pt/Al₂O₃ catalysts, but not as low as with Pt-Rh/Al₂O₃.

Chemical Vapor Deposition of Platinum Hexafluoroacetylacetonate inside KL Zeolite: A New Route to Nonacidic Platinum-in-Zeolite Catalysts

C. DOSSI, R. PSARO, A. BARTSCH, A. FUSI, L. SORDELLI, R. UGO, M. BELLATRECCIA, R. ZANONI and G. VLAIC, *J. Catal.*, 1994, 145, (2), 377-383
Pt/KL catalysts were prepared by selective introduction of Pt hexafluoroacetylacetonate inside KL zeolite channels via CVD in a flow of Ar at 70°C. *In situ* DRIFTS and EXAFS studies of the metal particles formed via removal of the volatile organic ligands under H₂ at 350°C, showed very small Pt clusters with a nucleophilic character. The nonacidic Pt/KL catalysts show high activity and selectivity in the conversion of methylcyclopentane to C₆H₆ at 500°C, and long life due to reduced coke formation.

Characteristics of Electron Migration in Oxide Catalysts. I. Formation of Paramagnetic Palladium Ions in Pd/Y₂O₃ and Pd/La₂O₃ Systems

I. N. FILIMONOV, I. A. IKONNIKOV and A. YU. LOGINOV, *Kinet. Catal.*, 1993, 34, (5), 900–908

The ionic state of a Pd compound stabilised in the oxide matrices of Y₂O₃ and La₂O₃ was characterised. Promoting Y₂O₃ and La₂O₃ with Pd was found to be similar to stabilisation by a large amount of paramagnetic Pd⁺ and Pd²⁺, which are usually found in the bulk and on the surface. Additionally, all Pd ions appeared to be co-ordinate-absorbed on the surface, thus resulting in extremely unstable oxidative-reductive reaction processes.

The Promotion Effects of Iron and Lithium on Ethanol Synthesis from Syngas over Rhodium-Based Catalysts

H.-Y. WANG, J.-P. LIU, J.-K. FU and Q.-R. CAI, *J. Fuel Chem. Technol.*, 1994, 21, (4), 337–343

The addition of Fe to Rh/SiO₂ catalyst used during EtOH synthesis from syngas resulted in ~ two fold increase in catalytic activity and 16.8% increase in EtOH selectivity without any decrease in acetaldehyde selectivity. Increased Rh dispersion and the effects of Fe²⁺ or Fe³⁺ on formyl intermediate formation and its hydrogenolysis cause the promotion of catalytic activity by Fe. The addition of Li to Rh/SiO₂ catalysts resulted in 11.5% increase in EtOH selectivity.

Formation of C₂ Oxygenates on Rhodium-Containing Catalysts during CO + H₂ Reactions. FTIR Study of Acetaldehyde Adsorption

D. DEMRI, J.-P. HINDERMANN, C. DIAGNE and A. KIENEMANN, *J. Chem. Soc., Faraday Trans.*, 1994, 90, (3), 501–506

The adsorption of CH₃CHO, CH₃COOH and crotonaldehyde was studied by FTIR on Rh/SiO₂ catalysts which were either unpromoted or promoted with CeO₂ and ZrO₂. Acetyl species were identified on the promoted catalysts. The role of the promoter is to stabilise the acetyl species. The Rh/SiO₂ produces almost pure CH₄ from the CO + H₂ reaction at atmospheric pressure. CH₃CHO is only physisorbed and heating gives CH₄ and CO without intermediates.

Hydrocarbons from Synthesis Gas: Selectivity Changes Induced by the Zeolite Matrix on the Metallic Function in Rh/Y Catalysts

G. J. SIRI, A. GUERRERO-RUIZ, I. RODRIGUEZ-RAMOS, P. TERREROS and J. L. G. FIERRO, *Appl. Catal. A: Gen.*, 1993, 107, (1), 59–71

RhNaY and RhHY zeolites were prepared either by ion exchange with RhCl₃, giving very small Rh aggregates within the supercages of faujasitic zeolite, or by Rh₂(CO)₁₂ sublimation under vacuum. The clusters became aggregated during reduction or on-stream mainly at the outer zeolite surface irrespective of the degree of protonation of the zeolite. The RhNaY catalyst was used for the conversion of CO/H₂ mixtures to low C alkenes and alkanes, mostly butenes/butanes.

Catalytic Properties of RhCl₃·3H₂O Immobilized on the Modified Poly(styrene-divinylbenzene) Copolymer in Aqueous Phase Hydroformylation of Propylene

K. S. RO and S. I. WOO, *J. Catal.*, 1994, 145, (2), 327–334
RhCl₃·3H₂O and RhCl(CO)(PPh₃)₂ immobilised on the poly(styrene-divinylbenzene) copolymer containing -CH₂P(C₆H₄SO₃H)₂ groups, Rh(III)/SPPS and Rh(I)/SPPS, respectively, were active and stable hydroformylation catalysts in aqueous phase. ³¹P NMR and FTIR studies showed that Rh(III)/SPPS and Rh(I)/SPPS have a similar structure and the Rh complexes are covalently anchored on the polymer. Their activity and selectivity increased with the increase of H₂ pressure. The rate increased with the increase of P_{CO} below 10 atm and decreased above 10 atm.

Oxidative Methane Conversion to Carbon Monoxide and Hydrogen at Low Reactor Wall Temperatures over Ruthenium Supported on Silica

Y. MATSUMURA and J. B. MOFFAT, *Catal. Lett.*, 1994, 24, (1, 2), 59–65

Oxidative CH₄ conversion to CO and H₂ was catalysed over Ru/SiO₂ at reactor wall temperatures as low as 400°C, when reactant flow rate is significantly high. The conversion of CH₄ and the yields of CO and H₂ increase with increase in the flow rate of reactants, while O₂ is always completely consumed. Addition of CO₂ to the reactant flow can increase the CO yield, which suggests that CO₂ acts as an oxidant and the catalyst surface temperature is high enough to allow thermal conversion of CH₄ via CO₂ and H₂O to occur.

HOMOGENEOUS CATALYSIS

Hydrogenation of Unsaturated Compounds in the Complex System Palladium-1,2-Diene. I. Catalytic Properties of Compounds Formed in the Pd(II)-Allene System

E. M. KHAR'KOVA, A. V. NOVIKOVA, L. E. ROZANTSEVA and V. M. FROLOV, *Kinet. Catal.*, 1993, 34, (5), 866–869
Complexes PdCl₂, K₂PdCl₄, Pd(AcAc)₂ with allene, 1,1-dimethylallene, trimethylene cyclohexane, isoprene in alcohol containing H₂O and in toluene, were found to be catalytically active during hydrogenation of unsaturated hydrocarbons, especially in isoprene. The highest hydrogenation rate of 1.8 × 10⁻³ mol/min was obtained in the presence of dimethylallene ligands containing complex catalyst.

Palladium(0)-Catalyzed Conversion of Vinyl Trifluoromethanesulfonates into α,β-Unsaturated Nitriles

E. PIERS and F. F. FLEMING, *Can. J. Chem.*, 1993, 71, (11), 1867–1872

Vinyl triflates were converted by a new general method into the corresponding α,β-unsaturated nitriles in good to excellent yields on treatment of each vinyl trifluoromethanesulphonate with dry LiCN in the presence of catalytic amounts of (Ph₃P)₂Pd and the crown ether 12-crown-4. Additional Pd improved the conversion.

Stereospecific Palladium/Copper Cocatalyzed Cross-Coupling of α -Alkoxy- and α -Aminostannanes with Acyl Chlorides

J. YE, R. K. BHATT and J. R. FALCK, *J. Am. Chem. Soc.*, 1994, 116, (1), 1-5

Stille-type cross-coupling between α -alkoxy(amino) stannanes and acyl chlorides co-catalysed by Pd and Cu salts, especially Pd(PPh₃)₂Cl₂ or Pd(PPh₃)₄, under mild, nearly neutral conditions produced α -hetero-substituted ketones in moderate to good yields. Coupling of chiral α -alkoxystannanes, which are easily obtainable by BINAL-H asymmetric reduction of acylstannanes, proceeds with ~98% retention of configuration. Aromatic acid chlorides gave the best yield.

Dehydrogenative Silylation of 1,5-Dienes with Hydrosilanes Catalyzed by RhCl(PPh₃)₃

F. KAKIUCHI, K. NOGAMI, N. CHATANI, Y. SEKI and S. MURALI, *Organometallics*, 1993, 12, (12), 4748-4750

Studies of the effect of the chelating substrate in catalytic reactions showed that reaction of 1,5-dienes with hydrosilanes involves dehydrogenative silylation in the presence of RhCl(PPh₃)₃ catalyst, yielding 1-silyl-1,5-dienes instead of the usual hydrosilylation products. The vinylsilane formation seems to be specific to 1,5-dienes. The RhCl(PPh₃)₃ catalysed reaction of 1,4-pentadiene or 1,6-heptadiene with HSiEt₂Me under identical conditions did not result in exclusive formation of similar 1-silyl 1,6-dienes.

Stereoselective Reduction of Disubstituted Aromatics on Colloidal Rhodium

K. NASAR, F. FACHE, M. LEMAIRE, J.-C. BÉZIAT, M. BESSON and P. GALLEZOT, *J. Mol. Catal.*, 1994, 87, (1), 107-115

Hydrogenation of disubstituted aromatic rings was achieved under mild conditions in a two-phase system in the presence of RhCl₃ and an amine phase transfer agent. The system was optimised for the 2-methylanisole reduction, with very small colloidal Rh particles stabilised by a suitable amine:Rh ratio. High chemoselectivity and high stereoselectivity to the *Z* isomer are obtained. *o*-Cresol derivatives were enantioselectively reduced with colloidal Rh stabilised and modified by chiral amines. Additionally, diastereoselective reduction was obtained with chiral auxiliaries bound to the substrate.

Selective Rhodium-Catalysed Oxidation of Alkanes to Alkyl Esters with Peracids

K. NOMURA and S. UEMURA, *J. Chem. Soc., Chem. Commun.*, 1994, (2), 129-130

Treating saturated hydrocarbons with H₂O₂ in trifluoroacetic acid in the presence of Rh salts at room temperature resulted in their selective transformation to the corresponding alkyl trifluoroacetates in good yields. [Rh₂O(OAc)₂(H₂O)₃]OAc was the most effective catalyst, followed by various Rh compounds such as [Rh(acac)₃], [RhCl(CO)₂]₂, Wilkinson's complex [RhCl(PPh₃)₃] and the Rh acetate dimer [Rh₂(OAc)₄]. A reaction pathway is proposed which uses the results from the reactivity order tertiary > secondary > primary, and the reaction's ionic nature.

Kinetic and Spectroscopic Study of the Hydrogen-Transfer Reaction from 2-Propanol to Cyclohexanone Catalyzed by [IrH₂(pz)(Hpz)(PPh₃)₂] (Hpz = pyrazole)

M. A. ESTERUELAS, M. P. GARCÍA, M. MARTÍN and L. A. ORO, *J. Mol. Catal.*, 1994, 87, (2-3), 151-160

A kinetic and spectroscopic investigation of the H transfer reaction from 2-propanol to cyclohexanone at 60°C catalysed by the title complex is discussed. Air was excluded from the reaction. The concentration of the catalyst has a linear relationship with the initial rate of the reduction. The rate of cyclohexanone formation was inhibited by the addition of pyrazole.

Concomitant Catalytic Transformations of Geminal Ethynyl and Hydroxy Groups of Steroids into Acetyl and Ester Functions with Retention of Configuration by [Ru(μ-O₂CH)(CO)₂(PPh₃)₂]

C. DARCEL, C. BRUNEAU, P. H. DIXNEUF and G. NEEF, *J. Chem. Soc., Chem. Commun.*, 1994, (3), 333-334

Steroids containing both hydroxy and ethynyl groups at C(17) have been selectively transformed by reaction with carboxylic acids, in the presence of [Ru(μ-O₂CH)(CO)₂(PPh₃)₂] complex catalyst, into β-oxopropyl esters which retain the configuration at C(17). The retention of configuration can be explained by addition of carboxylic acid to the Ru(II) activated C≡C bond, followed by intramolecular transesterification, according to a proposed catalytic cycle.

Selective Electrocatalytic Oxidations of Alkylaromatics Using a Polypyridyl Complex of Ruthenium(IV)

R. M. C. CARRIJO and J. R. ROMERO, *Synth. Commun.*, 1994, 24, (3), 433-440

Alkylaromatics were electrocatalytically oxidised with [Ru^{IV}O(bpy)(trpy)](ClO₄)₂ on toluene, *p*-methoxytoluene, ethylbenzene, *o*-, *m*-, and *p*-xylenes. Toluene and *p*-methoxytoluene yielded their respective carboxylic acids, but ethylbenzene produced acetophenone, without bond cleavage, in 66.5% yield. The xylenes were oxidised to their mono and diacids, *o*-toluic and phthalic acid, *m*-toluic and isophthalic acid, and *p*-toluic and terephthalic acid, respectively.

FUEL CELLS

Hydrous Oxide Species as Inhibitors of Oxygen Reduction at Platinum Activated Fuel Cell Cathodes

L. D. BURKE, J. K. CASEY, J. A. MORRISSEY and J. F. O'SULLIVAN, *J. Appl. Electrochem.*, 1994, 24, (1), 30-37

MeOH/air fuel cells require optimum performance of the air/oxygen cathode at ~0.8 V vs RHE, due to the inhibition, at above 0.8 V, of O₂ reduction on finely divided Pt deposits prepared by chemical reduction from aqueous solution. Thermally prepared Pt/C electrodes were more active in this region than those prepared by wet techniques. Hydrous oxide films which may be produced on Pt in 3.0 M H₂SO₄ at 60°C are quite stable on open circuit in the hot acid.

On the Role of Surface Functional Groups in Pt Carbon Interaction

P. L. ANTONUCCI, V. ALDERUCCI, N. GIORDANO, D. L. COCKE and H. KIM, *J. Appl. Electrochem.*, 1994, **24**, (1), 58–65

The interaction between Pt crystallites and C surface functional groups in Pt/C catalysts for PAFC has been studied. The area of the Pt surface depends on the amount of oxygenated groups on the C support. XPS shows the effect of the presence of O-C complexes on the Pt dispersion. The binding energy shifts in the XPS Pt 4f signals reflect the electron withdrawing nature of the neighbouring oxygenated C support.

Effect of Platinum Particle Size on the Performance of PAFC O₂ Reduction Electrocatalysts

N. GIORDANO, P. L. ANTONUCCI, E. PASSALACQUA, L. PINO, A. S. ARICÒ, V. ANTONUCCI, V. ALDERUCCI and V. RECUPERO, *Int. J. Hydrogen Energy*, 1994, **19**, (2), 165–168

The effects of mass activity on Pt surface area and the behaviour of some catalysts for PAFC in short-term endurance tests have been examined under controlled simulated conditions. Strictly controlled preparation of Pt/C materials, including functionalisation of the support, are needed for good activity and stability. Electrocatalyst activity increases as Pt particle size decreases.

Advances In Direct Oxidation Methanol Fuel Cells

S. SURAMPUDI, S. R. NARAYANAN, E. VAMOS, H. FRANK, G. HALPERT, A. LACONTI, J. KOSEK, G. K. SURYA PRAKASH and G. A. OLAH, *J. Power Sources*, 1994, **47**, (3), 377–385

A liquid feed direct MeOH fuel cell has been developed based on a proton-exchange membrane electrolyte and Pt/Ru and Pt-catalysed fuel and air/O₂ electrodes, respectively. The cell can deliver significant power outputs at 60–90°C. At operating temperatures < 88°C outputs in excess of 250 mA/cm² current density at cell voltage is ~ 0.5 V. Performance can be further improved by minimising the MeOH crossover rate.

CORROSION PROTECTION

Adsorbate-Catalyzed Dissolution in Inert Electrolyte: Layer-by-Layer Corrosion of Pd(100)-c(2 × 2)-I

J. A. SCHIMPF, J. B. ABREU and M. P. SORIAGA, *Langmuir*, 1993, **9**, (12), 3331–3333

The anodic dissolution of Pd in halide-free sulphuric acid, catalysed by a single adsorbed layer of I, was studied using a Pd(100) single crystal electrode having an ordered c(2 × 2) I adlattice. Pd dissolution only occurred on surfaces pretreated with I. The surface coverage and structure of the iodine adlattice were not affected by the corrosion reaction, which shows that anodic dissolution occurs on one interfacial metal-layer at a time. Layer-by-layer dissolution was also shown at the more closely packed Pd(111) electrode surface. The ordered I_(ads)-catalysed corrosion of Pd is independent of the surface crystallographic orientation.

CHEMICAL TECHNOLOGY

Methanation of Carbon Deposited Directly from CO₂ on Rhodium-Bearing Activated Magnetite

K. NISHIZAWA, H. KATO, K. MIMORI, T. YOSHIDA, N. HASEGAWA, M. TSUJI and Y. TAMAUURA, *J. Mater. Sci.*, 1994, **29**, (3), 768–772

The methanation reactivity of surface C deposited from CO₂ on the surface of Rh-bearing activated magnetite was studied, a typical composition being (Rh₂O₃)_{0.016}(Fe₃O₄)_{0.44}. The most active material contained 0.83 wt.% Rh and was prepared by impregnation at 60°C giving 98% CH₄ conversion at 300°C. Surface C contained elemental C (α-C) and polymerised C (β-C), with ratio depending on the density of C deposited. During the surface reaction the conversions of α-C and β-C to CH₄ was 0.34 and 0.53, respectively. Both forms of C are converted to CH₄ over Rh-bearing activated (α-C) magnetite.

ELECTRICAL AND ELECTRONIC ENGINEERING

A Novel Fabrication Process and Analytical Model for Pt/GaAs Schottky Barrier Mixer Diodes

V. KROZER and A. GRÜB, *Solid-State Electron.*, 1994, **37**, (1), 169–180

Pt/GaAs Schottky barrier diodes for millimetre and submillimetre wave mixing applications with near-ideal I/V characteristics were fabricated by application of new processing techniques. The fabrication process is based on the anodic pulse etching technique of GaAs in combination with an electrolytic *in situ* Pt deposition. The fabricated diodes show nearly ideal I/V and noise characteristics. The current spreading, the current dependent recombination velocity at the metal/semiconductor interface, the barrier lowering due to image forces and *n-n'* junction voltage were the most important effects encountered during Schottky diode operation in forward bias.

AlGaAs/GaAs Charge Injection Transistor/Negative Resistance Field-Effect Transistor Fabricated with Shallow Pd/Ge Ohmic Contacts

J.-T. LAI and J. Y.-M. LEE, *Appl. Phys. Lett.*, 1994, **64**, (3), 306–308

AlGaAs/GaAs charge injection transistor (CHINT)/negative resistance field effect transistor (NERFET) devices have been fabricated with Pd/Ge ohmic contacts, deposited by e-beam evaporation. The contact metal layers were annealed by rapid thermal annealing at 450–500°C for 1 min, giving a shallow ohmic contact and low specific contact resistivity, of the order of 10⁻⁴ Ωcm². Using Pd/Ge contacts and rapid thermal annealing, the metallisation of CHINT/NERFET becomes less critical, with simplified fabrication. Good device performance under NERFET mode and CHINT mode was achieved.