

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Desorption and Dissociation of Oxygen Admolecules on a Stepped Platinum (533) Surface

A. RAŘ and T. MATSUSHIMA, *Surf. Sci.*, 1994, **318**, (3), 89–96

The desorption and dissociation of O₂ admolecules were studied on a stepped Pt(533) surface by using thermal desorption combined with an isotope tracer. The desorption from the molecular adsorption state yielded two main peaks at 145 and 225 K, the latter peak being assigned to desorption from step sites. Most of the admolecules on step sites dissociate into adatoms in the subsequent heating at 150–250 K, but admolecules on terraces desorb without dissociation.

Superconductivity in PtSi Ultrathin Films

K. OTO, S. TAKAOKA, K. MURASE and S. ISHIDA, *J. Appl. Phys.*, 1994, **76**, (9), 5339–5342

Studies of normal and superconducting properties of PtSi films of thickness $d = 2$ –20 nm showed the superconducting transition on the thin films down to $d = 4$ nm. The systematic reduction of the transition temperature with decreasing d was explained by the localisation and Coulomb interaction effects on superconductivity. The temperature dependence of the upper critical field shows that the PtSi films behave as homogeneous superconductors.

The Pt-Sn Binary System

P. DURUSSEL, R. MASSARA and P. FESCHOTTE, *J. Alloys Compd.*, 1994, **215**, 175–179

The Pt-Sn binary system has been examined over the concentration range 1–2 at.% Sn. The five stoichiometric intermediate phases had generally higher melting points than previously indicated, for Pt₃Sn (1402°C) and PtSn (1276°C), and higher peritectic decomposition temperatures for Pt₂Sn₃ (898°C), PtSn₂ (748°C) and PtSn (540°C). The intermediate phase PtSn has a structure similar to PtSn₃ (*P6₃/mmc*) with a strictly stoichiometric composition.

Molecular Dynamics Simulations of Consolidation Processes during Fabrication of Nanophase Palladium

C.-L. LIU, J. B. ADAMS and R. W. SIEGEL, *NanoStruct. Mater.*, 1994, **4**, (3), 265–274

Dynamic consolidation processes which occur during fabrication of nanophase Pd from atom clusters have been simulated. Several phenomena, such as surface rounding, “neck” formation, void formation and shrinking, and cluster extrusion, were observed. The grain boundary structures are all very narrow and show only localised disorder. The effect of applied compressive pressures on the final structures of the nanophase materials during consolidation was shown.

Synthesis of Pd-doped SnO₂ Films on Silicon and Interaction with Ethanol and CO

M. LABEAU, A. M. GAS'KOV, B. GAUTHERON and J. P. SENATEUR, *Thin Solid Films*, 1994, **248**, (1), 6–11
Pure and Pd-doped polycrystalline SnO₂ films were prepared by a modified CVD method on oxidised <100> Si using the pyrolysis of an aerosol generated by ultrahigh frequency spraying of a volatile precursor solution. The deposition at 460–560°C controlled the growth rate, microstructure and composition of the films, and the moisture of the carrier gas. At low temperature the moisture increases the growth rate of SnO₂ but not of Pd. The heat treatments induce an increase of O and C concentration. Adding Pd to the films largely increases the gaseous adsorption, showing a maximum at low temperature.

Formation of Pd Silicides and Periodicity in Sputtered Pd/Si Nanometric Multilayers

L. WU, L. ZHOU, B. WANG, C. GAO, W. LIU and Z. WU, *Solid State Commun.*, 1994, **91**, (10), 817–819

Studies of the formation of Pd silicides and the periodicity in sputtered Pd/Si nanometric multilayers showed both Pd₂Si and PdSi in as-deposited Pd/Si multilayers with small periods of 1–5 nm, but only Pd₂Si for large periods. It is concluded that the roughness of the Pd/Si interfaces can reach about 2.0 nm and is related to the formation of the Pd silicides.

Ferromagnetism in an Intermetallic Compound Containing Palladium, Titanium and Aluminium

K.-U. NEUMANN, J. CRANGLE, J. G. SMITH, N. K. ZAYER and K. R. A. ZIEBECK, *J. Magn. & Magn. Mater.*, 1994, **137**, (3), 264–268

Ferromagnetism was observed in a ternary intermetallic Pd₂TiAl (1) compound in which the constituent elements do not order magnetically. The stoichiometric compound Pd₂TiAl has the cubic Heusler L₂ structure and a lattice parameter of 6.322 Å. The presence of a hysteresis in the magnetisation process confirms the existence of a spontaneous ferromagnetic moment. The ferromagnetism reported in (1) contrasts with the apparent antiferromagnetism in Pd₂TiIn and the small moment system, 0.005 μ_B, observed for Pd₂TiSn.

High Field Magnetization of UPd₂Al₃

K. ODA, T. KUMADA, K. SUGIYAMA, N. SATO, T. KOMATSUBARA and M. DATE, *J. Phys. Soc. Jpn.*, 1994, **63**, (8), 3115–3121

Studies of the high field magnetisation of antiferromagnetic heavy fermion material UPd₂Al₃ at ≤ 50 T showed a clear metamagnetic step at 18 T along the *a*-axis at 1.3 K. The angular dependence of step-magnetisation shows a large anisotropy in the *ac*-plane. The spin system can be described by the *XY*-spin model except for very small anisotropy in the *c*-plane.

Magnetic Ordering in U_2Pd_2In and U_2Pd_2Sn

A. PURWANTO, R. A. ROBINSON, L. HAVELA, V. SECHOVSKÝ, P. SVOBODA, H. NAKOTTE, K. PROKES, F. R. DE BOER, A. SERET, J. M. WINAND, J. REBIZANT and J. C. SPIRLET, *Phys. Rev. B.*, 1994, **50**, (10), 6792–6801

Studies of the tetragonal intermetallic compounds U_2Pd_2In and U_2Pd_2Sn showed them to order antiferromagnetically at 36 and 41 K, respectively, and to have enhanced electronic specific heat coefficients γ of 393 and 203 mJ/mol K^2 , respectively. At low temperature, the nearest-neighbour U-U spacing is along the c axis in both compounds, but in U_2Pd_2Sn the in-plane U-U distance was shorter at room temperature. This crossover is due to motion of the U atoms within the cell rather than anisotropy of the thermal contraction. At 10 K, the magnetic moments are $(1.6 \pm 0.2)\mu_B$ and $(2.0 \pm 0.1)\mu_B$ per U atom in U_2Pd_2In and U_2Pd_2Sn , respectively.

Electrical Resistivity and Thermopower Studies of $Ce(Rh_{1-x}Ru_x)_2Si_2$ Compounds with $0 \leq x \leq 0.4$

R. P. PINTO, M. E. BRAGA, M. M. AMADO, J. B. SOUSA, B. CHEVALIER and J. ÉTOURNEAU, *J. Alloys Compd.*, 1994, **215**, 217–221

Electrical resistivity (ρ) and thermopower (S) were measured on both $LaRh_2Si_2$ and the heavy fermion compounds $Ce(Rh_{1-x}Ru_x)_2Si_2$ at 3.5–300 K. The ρ (T) and $S(T)$ curves for $LaRh_2Si_2$ showed that the thermopower and electrical resistivity in $Ce(Rh_{1-x}Ru_x)_2Si_2$ mainly reflect the rather anomalous scattering arising from the Ce ions. Transport properties of isomorphous $LaRh_2Si_2$ were studied for comparison.

Polycrystalline Iridium Silicide Films. Phase Formation, Electrical and Optical Properties

J. SCHUMANN, D. ELEFANT, C. GLADUN, A. HEINRICH, W. PITSCHKE, H. LANGE, W. HENRION and R. GRÖTZSCHEL, *Phys. Status Solidi (a)*, 1994, **145**, (2), 429–439

Electrical and optical properties of thin Ir_xSi_{1-x} films ($0.25 \leq x \leq 0.55$) prepared by DC-magnetron co-deposition and annealed at 400–1170 K, were studied as a function of the crystallisation. The dominant phases were $IrSi$, Ir_3Si , Ir_5Si_3 , and $IrSi_2$, and films having the semiconducting compound Ir_3Si , as main phase showed a large thermopower only in a small composition range depending on the grain size. The optical gap of Ir_3Si was determined to be 1.56 eV.

The Nuclear Magnetic Resonance of ^{99}Ru and ^{101}Ru in Hexagonal Close-Packed Ruthenium Metal

A. BURGSTALLER, J. VOITLÄNDER and H. EBERT, *J. Phys. Condens. Matter*, 1994, **6**, (40), 8335–8340

The NMR of ^{99}Ru and ^{101}Ru was observed in hexagonal close packed Ru metal and the field spectra show the characteristics of quadrupolar disturbed NMR. The measurement of the spin-lattice relaxation of the isotopes ^{99}Ru and ^{101}Ru , carried out at 4.2 K, yielded spin-lattice relaxation times of 3.7 ± 0.2 s and 3.1 ± 0.2 s, respectively. The rather high positive isotropic Knight shift is due to the Van Vleck contribution, which is also responsible for the strong anisotropy.

Nanocrystalline B2 Type $Ru_{40}Al_{60}$ and Ru Powders Produced by Mechanical Alloying and Leaching

Y. XU, S. A. MAKHLOUF, E. IVANOV, K. WAKOH, K. SUMIYAMA and K. SUZUKI, *NanoStruct. Mater.*, 1994, **4**, (4), 437–444

Nanocrystalline B2 type $Ru_{40}Al_{60}$ and Ru were obtained by mechanically alloying Ru and Al powder mixtures followed by leaching Al. About 90% of Al atoms are removed by basic 30 wt.% NaOH, leaving the B2 structure. The leached Ru powder is very active and explosive in contact with air, but after annealing at 873 K for 1 h, it transforms into the stable h.c.p. structure. The solid solubility of 14 at.% Al in nanocrystalline h.c.p. Ru exceeds that in conventional bulk h.c.p. Ru. As-milled and leached samples were nonmagnetic.

Semiconducting Behavior of the Intermetallic Compound Al_2Ru

P. VOLKOV and S. J. POON, *Europhysics Lett.*, 1994, **28**, (4), 271–276

Transport studies of polycrystalline Al_2Ru showed it to be a semiconductor, even at low temperature. The high DC conductivity ratio $\sigma(300\text{ K})/\sigma(0.46\text{ K}) \sim 50$ and low conductivity $\sigma(0.46\text{ K}) = 0.21/\Omega\text{ cm}$ are anomalous for metal-based alloys. At temperatures > 500 K, σ shows an activated behaviour which indicates an energy gap, in good agreement with band structure calculations and optical-conductivity results.

Structural and Electronic Properties of the Dilute Magnet $Sr_{1-x}La_xZn_{1-x}Ru_xO_4$ ($1/3 \leq x \leq 2/3$)

S. H. KIM and P. D. BATTLE, *J. Solid State Chem.*, 1994, **112**, (2), 262–269

The solid solution $Sr_{1-x}La_xZn_{1-x}Ru_xO_4$ has the tetragonal K_2NiF_4 structure with a disordered arrangement of Zn^{2+} and Ru^{2+} over the octahedral sites. The sample with $x = 1/3$ is paramagnetic over the temperature range $6 < T < 296$ K. With increases in Ru concentration, short-range antiferromagnetic interactions between Ru^{2+} ions became more important. The magnetic susceptibility showed a maximum at low temperatures when x was larger than the percolation threshold for a nearest-neighbour square lattice.

CHEMICAL COMPOUNDS

Heterometallic Binuclear Complexes Having the Mercury-Platinum Bond as a Source of a Platinum Carbenoid in Reactions with Fullerene-60

V. V. BASHILOV, B. L. TUMANSKII, P. V. PETROVSKII and V. I. SOKOLOV, *Izv. Akad. Nauk Rossii, Ser. Khim.*, 1994, (6), 1131–1134

The cleavage of two σ bonds and the formation of $(\eta^2-C_{60})Pt(PPh_3)_2$ occur in a new reaction between fullerene-60 and binuclear heterometallic compounds, with a Hg-Pt bond. Complex *trans*- $Ph_2CHCH_2HgPt(PPh_3)_2Br$ reacts much faster than *cis*-(CF_3) $_2CFHgPt(PPh_3)_2CH=CPh_2$, which gives a Pt-centred radical under photolytic conditions. A Pt-fullerenyl radical *cis*- $C_{60}Pt(PPh_3)_2R$ was identified by EPR spectroscopy.

Synthesis and Structure of Li_3RhH_6 – a Ternary Hydride with Isolated $[\text{RhH}_6]^{3-}$ Octahedra

W. BRONGER, M. GEHLEN and G. AUFFERMANN, *Z. Anorg. Allg. Chem.*, 1994, **620**, (11), 1983–1985

The ternary Rh hydride Li_3RhH_6 was prepared by reacting Li hydride with Rh under a H_2 pressure of 80 bar. The atomic arrangement is isotypic to the Na_3RhH_6 structure type. The crystal structure contains isolated $[\text{RhH}_6]^{3-}$ octahedra, which are separated by the Li ions. X-ray studies on powdered samples and elastic neutron diffraction experiments on the deuterated compound showed that it crystallises in space group $Pnma$ with $Z=4$.

Crystal Growth and Properties of Novel Ternary Transition Metal Chalcogenide Compounds $[\text{Ir}_x\text{Ru}_{1-x}\text{S}_2]$ ($0.005 < x < 0.5$)

H. COLELL, N. ALONSO-VANTE, S. FIECHTER, R. SCHIECK, K. DIESNER, W. HENRION and H. TRIBUTSCH, *Mater. Res. Bull.*, 1994, **29**, (10), 1065–1072

Pure semiconducting pyrite phases RuS_2 and IrS_2 , and mixed pyrite phases $\text{Ir}_{0.007-x}\text{Ru}_{1-x}\text{S}_2$ ($0 < x < 1$), prepared in powder form, were used to produce single crystals by chemical vapour transport and high temperature solution growth from Bi fluxes. $\text{Ir}_x\text{Ru}_{1-x}\text{S}_2$ ($0.005 < x < 0.5$) crystals were synthetically grown, resulting in a S deficiency. The incorporation of Ir in the RuS_2 matrix induced a degenerate character in these mixed-phase single crystals, at carrier concentration of $> 10^{20}/\text{cm}^3$. Thus a new class of ternary Ir-Ru-S compounds has been synthesised for the first time. They have potential applications for photovoltaic solar energy use.

The First Ruthenium Carbonyl Derivative of Fullerene: $(\eta^5\text{-C}_{60})\text{Ru}(\text{CO})_4$

M. RASINKANGAS, T. T. PAKKANEN and T. A. PAKKANEN, *J. Organomet. Chem.*, 1994, **476**, (1), C6–C8

$\text{Ru}(\text{CO})_4$ solution was added in mole ratio 1 : 1 to a toluene solution of C_{60} under N_2 to yield a 1 : 1 adduct $(\eta^5\text{-C}_{60})\text{Ru}(\text{CO})_4$ (1). It appears that $(\eta^5\text{-C}_{60})\text{Ru}(\text{CO})_4$ is more stable than $(\eta^5\text{-C}_{60})\text{Fe}(\text{CO})_4$ (2), since Ru has stronger binding to this fullerene than does Fe. The structures of (1) and (2) are similar, and they have very similar IR and ^{13}C MNR spectra. The synthesis and spectroscopic characterisation of compound (1) is described.

Auration of Ruthenocene: Synthesis and Molecular Structure of Mono- and Diaurated Derivatives

M. N. NEFEDOVA, I. A. MAMEDYAROVA, V. I. SOKOLOV, E. I. SMYSLOVA, L. G. KUZ'MINA and K. I. GRANDBERG, *Izv. Akad. Nauk Rossii, Ser. Khim.*, 1994, (7), 1335–1337
Ruthenocene, like ferrocene, yields the *gem*-diaurated derivative $\text{CpRuC}_2\text{H}_4(\text{AuPPh}_3)_2\text{BF}_4$ (1) when reacted with $(\text{Ph}_3\text{PAu})_2\text{O}^+\text{BF}_4^-$. Treatment of (1) with PPh₃ gives $\text{CpRuC}_2\text{H}_4\text{AuPPh}_3$. It is suggested that the order of interaction of Ru–Au and the corresponding order of positively charged transport to Ru is higher than that of Fe–Au. X-ray analysis showed an important interaction between Ru–Au in the diaurated derivative.

Preparation of Ultrafine RuO_2 – IrO_2 – TiO_2 Oxide Particles by a Sol-Gel Process

Y. TAKASU, S. ONOUE, K. KAMEYAMA, Y. MURAKAMI and K. YAHIKOZAWA, *Electrochim. Acta*, 1994, **39**, (13), 1993–1997

Ultrafine RuO_2 – IrO_2 – TiO_2 ternary oxide particles with different content ratios were prepared by a sol-gel method with metal alkoxides. Only a RuO_2 -rich sample contained a mixture of rutile-type oxide phase and a metallic phases. However, for Ti-deficient samples, uniform solid solutions with rutile-type oxide were prepared after calcination in air at 450°C, while mixtures of heterophase oxide particles were prepared for the other samples. These powdery oxides can aid development of active catalysts and explain the phase diagram.

ELECTROCHEMISTRY

Chemically Modified Electrodes by Nucleophilic Substitution of Chlorosilylated Platinum Oxide Surfaces

C.-H. CHEN, J. E. HUTCHISON, T. A. POSTLETHWAITE, J. N. RICHARDSON and R. W. MURRAY, *Langmuir*, 1994, **10**, (9), 3332–3337

Chlorosilylated Pt oxide electrode surfaces were generated by reaction of SiCl_4 vapour with an electrochemically prepared monolayer of Pt oxide. Various nucleophilic agents, such as alcohols, amines, thiols, etc., can be used to displace chloride and thus functionalise the metal surface. Electroactive surfaces prepared with ferrocene MeOH as the nucleophile show that derivatisation by small molecules can achieve coverages of the order of a full monolayer.

Electroreduction of Carbon Dioxide on Palladium Electrodes at Potentials Higher than the Reversible Hydrogen Potential

B. I. PODLOVCHENKO, E. A. KOLYADKO and S. LU, *J. Electroanal. Chem.*, 1994, **373**, (1–2), 185–187

The electroreduction of CO_2 was observed on electrodes of dispersed electrodeposited Pd on Pt wire net and on Pt plate at potentials more positive than the reversible H potential, at pH 8–10, with the HCOO^- current yield close to 100%. The adsorbed H atoms were assumed to participate in the slow stage of the electroreduction of HCO_2 (CO_2) to HCOO^- .

Stabilization of the Redox Polymer $[\text{Os}(\text{bipy})_2(\text{PVP})_{10}\text{Cl}]\text{Cl}$ by in Situ Chemical Cross-Linking

A. P. DOHERTY, T. BUCKLEY, D. M. KELLY and J. G. VOS, *Electroanalysis*, 1994, **6**, (7), 553–560

The redox polymer $[\text{Os}(\text{bipy})_2(\text{PVP})_{10}\text{Cl}]\text{Cl}$ where bipy is 2,2'-bipyridyl and PVP is poly-4-vinylpyridine, was physically stabilised by chemical cross-linking at various levels via the solid-state reaction with the cross-linking agents *p*-dibromobenzene, 1,5-dibromopentane and 1,10-dibromodecane. The stability of the polymer films was increased, compared to uncross-linked polymer, when under severe hydrodynamic operation, such as in thin-layer flow cells. The charge transport properties of the redox polymer were maintained or improved by cross-linking.

PHOTOCONVERSION

Photochemical C-H Bond Activation of Methane on a Pt(111) Surface

Y. A. GRUZDKOV, K. WATANABE, K. SAWABE and Y. MATSUMOTO, *Chem. Phys. Lett.*, 1994, **227**, (3), 243–247

CH₄ adsorbed on a Pt(111) surface desorbs at ~ 70 K. However, after the CH₄-precovered surface was irradiated with 193-nm photons, the intensity of the thermal desorption peak decreased and a new CH₃ peak at ~260 K grew with the accumulated number of photons. CH₄ on Pt(111) was photodissociated to yield a chemisorbed CH₃ radical and an adsorbed H atom as products. The total cross section of the photochemical process was ~ 1.5 × 10⁻¹⁹ cm².

The Influence of Conditions on the Yield of an Aldehyde in the Photocatalytic Carbonylation of Pentane in the Presence of the System Rh₂Cl₂(CO)₄+PMe₃

N. K. KHANNANOV, G. N. MENCHIKOVA and E. A. GRIGORYAN, *Izv. Akad. Nauk Rossii, Ser. Khim.*, 1994, (6), 1013–1017

Studies of the photocatalytic carbonylation of pentane in Rh₂Cl₂(CO)₄+PMe₃, displayed a maximum dependence for the aldehyde yield on the CO and PMe₃ concentrations. The increase in aldehyde yield with increasing CO pressure is closely related to the increase in the carbonylation rate and the decrease in aldehyde photodecomposition. The rate of photocatalytic carbonylation of pentane in this system is 20 times higher than that in RhCl(PMe₃)₂CO.

Reductive Quenching of the Excited States of Ruthenium(II) Complexes Containing 2,2'-Bipyridine, 2,2'-Bipyrazine, and 2,2'-Bipyrimidine Ligands

H. SUN and M. Z. HOFFMAN, *J. Phys. Chem.*, 1994, **98**, (45), 11719–11726

The reductive quenching of the luminescent excited states of Ru(bpy)₃, m-z(bpm)_m(bpz)_z²⁺ (bpy = 2,2'-bipyridine, bpm = 2,2'-bipyrimidine, bpz = 2,2'-bipyrazine, m and z = 0, 1, 2, 3 and m + z ≤ 3) by aromatic amines and methoxybenzenes as non-sacrificial electron donors and by C₂O₄²⁻, EDTA and TEOA as sacrificial donors in aqueous, acetonitrile, and propylene carbonate solution was studied by laser flash photolysis. An E⁰ for the irreversible oxidation of TEOA (-0.84 ± 0.12 V vs. NHE) in acetonitrile was obtained.

Intramolecular Transfer of ³MLCT Excitation Energy in [Ru(bpy)₃]²⁺

H. RIESEN, Y. GAO and E. KRAUSZ, *Chem. Phys. Lett.*, 1994, **228**, (6), 610–615

The rate of ³MLCT excitation energy transfer between the two crystallographically equivalent ligand units of [Ru(bpy)₃]²⁺ in [Zn(bpy)₃](ClO₄)₂ lattice was measured by time-resolved luminescence line-narrowing studies. At 1.8 K, the transfer rate is ~ 1 × 10⁹/s in the second lowest-excited level II. The slow transfer rate is consistent with a small excitation exchange interaction between the equivalent metal-ligand units.

Semiconductor Sensitization by Ru₂S Colloids on TiO₂ Electrodes

M. ASHOKKUMAR, A. KUDO, N. SAITO and T. SAKATA, *Chem. Phys. Lett.*, 1994, **229**, (4, 5), 383–388

RuS₂ (n-type) colloids, prepared by a new technique using diluted RuS₂ colloidal suspension in sulpholane, displayed green photoluminescence. The RuS₂-coated TiO₂ electrodes showed spectral sensitisation caused by RuS₂ with an increase in the photocurrent response of TiO₂ towards the longer wavelength spectral region. The photocurrent action spectra of these electrodes qualitatively suggests a band gap of ~ 2.2–2.8 eV for RuS₂ which is wider than that of the bulk material, showing size quantisation effects. A flat-band potential of ~ -0.15 V (vs. Ag/AgCl) was observed.

ELECTRODEPOSITION AND SURFACE COATINGS

Electrolytic Deposition of Palladium-Iron Alloys

P. JUZIKIS, M. U. KITTEL and CH. J. RAUB, *Plat. Surf. Finish.*, 1994, **81**, (8), 59–62

Pd-alloy layers were produced from an ammoniacal bath containing Pd(II) and Fe(III) chlorides, with sulphosalicylic acid as a complexing agent. In the range of the limiting solid solutions of Pd- and Fe-rich alloy, the layers were crystalline, while in the medium concentration range they showed a multiphase structure with at least one phase being exceptionally distorted. Non-metallic impurities were ~100 ppm and H content and coercive force displayed a maximum near 75 wt.% Pd. The coercive forces of the as-deposited alloys were ~ 100–150 Oe.

Crack-Free Rhodium Deposition on Brass Substrates

M. L. DAS, *Metal Finish.*, 1994, **92**, (10), 12

A Rh plating solution containing 15 g/l Rh was prepared by dissolving concentrated Rh sulphate in distilled H₂O at 30°C and a current density of 7.5 A/dm² was applied. A brass panel was electroplated with Rh for 30 min using a Pt metal sheet as anode. Al, Mg and Se were added to the plating solution to reduce cracks. With selenic acid in the plating bath, the deposit became completely crack-free, but the surface roughened. Roughness could be removed by polishing.

APPARATUS AND TECHNIQUE

Capacitive Air-Fuel Ratio Sensor

R. E. HETRICK and A. L. SCHAMP, *Sens. Actuators B*, 1994, **21**, (1), 5–10

Air-fuel ratio in automotive exhaust can be monitored by capacitive measurement of the reversible change in the work function of Pt at stoichiometry. This change, which is as much as 0.7 V, occurs at elevated temperatures when the Pt is alternately exposed to dilute mixtures of oxidising (O) and reducing (HC and related molecules) species that are rich or lean of their stoichiometric ratio. It can be electrically monitored by the Kelvin vibrating capacitor method.

Investigations of Platinized and Rhodinized Carbon Electrodes for Use in Glucose Sensors

S. F. WHITE, A. P. F. TURNER, R. D. SCHMID, U. BILITEWSKI and J. BRADLEY, *Electroanalysis*, 1994, 6, (8), 625–632
Studies of graphite electrodes modified by the electrodeposition of either Pt or Rh showed that platinised C electrodes could directly oxidise glucose at a potential of +350 mV (vs. Ag/AgCl). H₂O₂ was detected at +400 mV using glucose enzyme electrodes, with glucose oxidase immobilised in hydroxyethylcellulose. The sensors had a linear range of 0.1–25 mM glucose and a slope of 8 nA/mM. Glucose sensors using rhodinised electrodes operating at +400 mV, had a linear range of 0.1–2 mM and a slope of 21 nA/mM glucose.

A New Hydrogen Sensor Using a Polycrystalline Diamond-Based Schottky Diode

W. P. KANG, Y. GURBUZ, J. L. DAVIDSON and D. V. KERNS, *J. Electrochem. Soc.*, 1994, 141, (8), 2231–2234
A new polycrystalline diamond-based H-sensitive Schottky diode using layered Pd/undoped diamond/*p*-doped diamond has been fabricated and the H sensing performance was analysed at 27–85°C. The H sensitivity was high, repeatable and reproducible. The study showed that the barrier height of Pd-diamond Schottky diode increases upon H adsorption. This leads to a change in the I-V characteristics from near ohmic to rectifying behaviour. This new H sensing technology should have many applications due to its reproducibility, sensitivity and performance over a wide temperature range, including room temperature.

Screen-Printed Glucose Strip Based on Palladium-Dispersed Carbon Ink

J. WANG and Q. CHEN, *Analyst*, 1994, 119, (4), 1849–1851

Pd-dispersed graphite ink was used for screen printing a disposable biosensor for glucose. The dispersed Pd particles decreased the overvoltage for the oxidation of the enzymically liberated H₂O₂ and greatly enhanced sensitivity and selectivity. The electrocatalytic behaviour was characterised, the sensor operation optimised and the analytical performance reported. The possibility of using metallised graphites for mass producing amperometric biosensors is discussed.

Luminescence Lifetime-Based Sensor for Relative Air Humidity

D. B. PAPKOVSKY, G. V. PONOMAREV, S. F. CHERNOV, A. N. OVCHINNIKOV and I. N. KUROCHKIN, *Sens. Actuators B*, 1994, 22, (1), 57–61

Sensitive coatings were developed for fibre optic sensors based on phosphorescent H₂O-soluble Pt- and Pd-porphyrin dyes contained in monomolecular thin solid Langmuir-Blodgett films. These were transferred onto solid supports. The coatings have intense long-decay phosphorescence in ambient air, and are sensitive to the environmental H₂O content, such as the relative humidity (RH) of air. The studied coatings have been applied to luminescence lifetime-based sensing of RH, and a highly reproducible prototype fibre-optic device has been produced.

Highly Selective Membrane-Free, Mediator-Free Glucose Biosensor

J. WANG, J. LIU, L. CHEN and F. LU, *Anal. Chem.*, 1994, 66, (21), 3600–3603

Highly selective amperometric glucose biosensors were produced by coupling the catalytic action of Rh microparticles with C paste/glucose oxidase probes. The dispersed Rh particles displayed efficient and preferential electrocatalytic activity toward the liberated H₂O₂ species and allowed cathodic detection of the glucose substrate at –0.10 V, with no interference from easily oxidisable constituents.

HETEROGENEOUS CATALYSIS

A Model for the Enantioselective Hydrogenation of Pyruvate Catalysed by Alkaloid-Modified Platinum

K. E. SIMONS, P. A. MEHEUX, S. P. GRIFFITHS, I. M. SUTHERLAND, P. JOHNSTON, P. B. WELLS, A. F. CARLEY, M. K. RAJUMON, M. W. ROBERTS and A. IBBOTSON, *Recl. Trav. Chim. Pays-Bas*, 1994, 113, (10), 465–474

Molecular modelling studies for the above reaction showed that a highly specific 1:1 interaction between cinchonidine and pyruvate explains the observed enantioselectivity, and the product of this 1:1 interaction is a suitable precursor to the H-bonded state required for the increased rate which accompanies enantioselective reaction over cinchona-modified Pt. Catalysts modified and used only under anaerobic conditions showed little activity and enantioselectivity showing the crucial role of O in successful catalyst preparation. Various configurations of ephedrine, D- and L-histidine, etc., were studied as modifiers for supported Pt.

Influence of Operational Variables on the Catalytic Behavior of Pt/Alumina in the Slurry-Phase Hydrogenation of Phenol

M. A. GUTIÉRREZ-ORTIZ, A. CASTAÑO, M. P. GONZÁLEZ-MARCOS, J. I. GUTIÉRREZ-ORTIZ and J. R. GONZÁLEZ-VELASCO, *Ind. Eng. Chem. Res.*, 1994, 33, (11), 2571–2577

Hydrogenation of phenol in the liquid phase was studied in a stirred tank reactor with highly dispersed Pt/ γ -Al₂O₃ catalyst prepared by adsorption from an aqueous solution of H₂PtCl₆, which was suspended as a slurry. Stirring rates > 9 Hz, catalyst particle size < 50 μ m, and catalyst weight < 0.5 g ensures a chemically-controlled regime during catalysis. Increasing the total pressure resulted in an almost linear increase in activity and decrease in selectivity.

Effects of Metal Accessibility on Catalytic Performance for Pt/H-Mordenite

B. A. LERNER, B. T. CARVILL and W. M. H. SACHTLER, *Catal. Today*, 1994, 21, (1), 23–36

When calcined precursors of 0.5% Pt/H-mordenite catalysts were exposed to H₂O vapour before reduction, they displayed enhanced catalytic activity for methylcyclopentane conversion, and larger Pt particles were formed after reduction. Hydrated Pt ions are mobile and are formed near the mouth of the zeolite pores where the concentration of precursor ions is high.

The Role of Rh on Pt-Based Catalysts: Structure Sensitive NO + H₂ Reaction on Pt(110) and Pt(100) and Structure Insensitive Reaction on Rh/Pt(110) and Rh/Pt(100)

A. SASAHARA, H. TAMURA and K.-I. TANAKA, *Catal. Lett.*, 1994, 28, (2-4), 161-166

The catalytic activity of the Pt(110) surface for the NO + H₂ reaction was less than that of the Pt(100) surface, but the catalytic activity of the Rh deposited Pt(110) surface was almost equal to that of the Rh deposited Pt(100) surface. The reaction of NO + H₂ on Pt(110) and Pt(100) surfaces is highly structure sensitive, but becomes structure insensitive on deposition of Rh atoms. The formation of the Rh-O/Pt overlayer during catalysis was responsible for the structure insensitive catalysis of Rh on Pt-based catalysts. This active overlayer is responsible for the catalytic activity of Pt-Rh three-way catalysts.

Enhancement of Pt-Sn/Al₂O₃ Catalyst Stability for Butane Dehydrogenation by Modification with Sm and Li

L. WANG, L. LIN, T. ZANG and H. CAI, *React. Kinet. Catal. Lett.*, 1994, 52, (1), 107-111

Studies of the effects of modification, by Sm and Li, on the stability of Pt-Sn/Al₂O₃ catalysts showed that Pt crystallite dispersion on the support can be promoted by both Sm and Li. When Sm was incorporated into the Pt-Sn/Al₂O₃ catalyst carbonisation was inhibited and the catalyst lifetime was prolonged.

Effect of Dispersion of Palladium on the Selective Hydrogenation of Acetylene in Ethane-Ethylene Fraction

G. D. ZAKUMBAEVA, N. F. TOKTABAIEVA, A. ZH. KUBASHEVA and I. G. EFREMEENKO, *Neftekhimiya*, 1994, 34, (3), 258-267

The effect of dispersion of Pd particles in 1.0-0.03% Pd/Al₂O₃ catalysts on the activity and selectivity of the catalyst was studied during acetylene hydrogenation in ethane-ethylene fractions. The majority (70-90%) of Pd particles used in the catalysts were 9; 15; 25; or 75 Å in diameter. Catalysts with Pd particles of 75 Å in diameter have many properties of the metal, so are capable of H diffusion. It is shown that an increase in Pd particle size led to a decrease in selectivity of catalyst during the above reaction.

Stabilisation of Palladium Metal Function of Oxide Supported Palladium Catalyst during the Hydrogenolysis of Chlorofluorocarbons

M. J. SWEETMAN and J. THOMSON, *J. Chem. Soc., Chem. Commun.*, 1994, (20), 2385-2386

Pd/ZnO catalysts supported on γ -Al₂O₃ showed enhanced catalytic activity and stability towards deactivation by halogen adsorption during the hydrogenolysis of 1,1,2-trichlorotrifluoroethane, when compared to Pd/C and Pd/ γ -Al₂O₃ systems. Catalysts with Pd:ZnO ratios of 0.25, 0.5, 1.0 and 2.0 were tested. The catalytic activity and selectivity of the Pd/ZnO catalyst towards complete dechlorination of the chlorofluorocarbon substrate is dependent on an optimum stoichiometric ratio of the two catalyst components.

Pd,Ni₉₅ and Pd₅Ni₉₅: Pd Surface Segregation and Reactivity for the Hydrogenation of 1,3-Butadiene

P. MIEGGE, J. L. ROUSSET, B. TARDY, J. MASSARDIER and J. C. BERTOLINI, *J. Catal.*, 1994, 149, (2), 404-413

Pd was found to segregate on Pd,Ni₉₅ and Pd₅Ni₉₅. After annealing and stabilising at 870 K, the external Pd concentration reached 20 and 50 at.%, respectively. On both solids, the Pd segregation displayed quite steep concentration profiles. The study of activities for 1,3-butadiene hydrogenation showed that the alloys were either equivalent or more active than pure Pd, while the selectivities for butenes remained close to unity. "Active sites" of small ensembles of Pd atoms electronically modified by the surrounding Ni atoms is proposed.

A Polymer-Bound Bidentate-Phosphine-Palladium Complex as a Catalyst in the Heck Arylation

P.-W. WANG and M. A. FOX, *J. Org. Chem.*, 1994, 59, (18), 5358-5364

Polymer-supported 1,2-bis(diisopropylphosphino)benzene Pd(II) complex catalyst was developed for a Heck arylation by incorporating a bidentate phosphine ligand onto a polystyrene backbone. The catalyst displayed high turnover number, ease of recycling without loss of activity, moderate efficiency with reaction rate being slightly slower than with Pd(OAc)₂/PPh₃, easy separation of product from the catalyst and stability for handling in air. Dimerisation of the reactive Pd(0) sites, which may occur during coupling under homogeneous conditions, is suppressed with this Pd catalyst.

Mechanism of the Wacker Oxidation of Alkenes over Cu-Pd-Exchanged Y Zeolites

P. H. ESPEEL, G. DE PEUTER, M. C. TIELEN and P. A. JACOBS, *J. Phys. Chem.*, 1994, 98, (44), 11588-11596

The catalytic potential of CuPd zeolites with faujasite topology in the Wacker oxidation of 1-alkenes with dioxygen is reported and compared to that of a homogeneous PdCl₂-CuCl₂ salt solution. From *in situ* spectroscopy measurements an active site is proposed, consisting of a trinuclear Cu-O-Pd-O-Cu cationic complex, and also a catalytic cycle for the Wacker oxidation in which the reoxidation of Cu⁺ by dioxygen or of Pd⁰ by zeolite Cu²⁺, is rate determining.

Preparation and Catalytic Properties of NR₄⁺-Stabilized Palladium Colloids

H. BÖNNEMANN, R. BRINKMANN and P. NEITELER, *Appl. Organomet. Chem.*, 1994, 8, (4), 361-378

NR₄⁺-stabilized Pd colloids with mean particle diameter of 1.8-4.0 nm, which can be isolated totally redispersed, and are easily handled in unusually high concentrations, were prepared as both heterogeneous and homogeneous catalysts. The standard activity of a charcoal catalyst with 5% colloidal Pd considerably exceeded the activity of the conventional catalyst. The lifetime of these catalysts, isolated from the reduction of [N(octyl)₄]₂PdCl₂Br₂ with H₂, was superior to conventionally prepared Pd/charcoal catalysts.

The Promoter Function of Molybdenum in Rh/Mo/SiO₂ Catalysts for CO Hydrogenation

J. Y. SHEN, T. MATSUZAKI, T. HANAOKA, K. TAKEUCHI and Y. SUGI, *Catal. Lett.*, 1994, **28**, (2-4), 329-336

FT-IR, chemisorption and CO hydrogenation of a number of Rh/Mo/SiO₂ catalysts with fixed Rh and varying Mo contents showed that the addition of Mo to Rh/SiO₂ suppresses the linear and bridged CO species, but promotes the twin CO species. The Mo promoter appears to work via stabilisation of Rh ions and the coverage of Rh sites by forming oxygenates and shifting the selectivity from HC to oxygenates.

Hydrogenation of Carbon Monoxide on Polymetallic Ruthenium Containing Catalysts

G. D. ZAKUMBAEVA, L. B. SHAPOVALOVA and E. S. MAKHMOTOV, *Kinet. Katal.*, 1994, **35**, (3), 400-405

Studies of the relationship of the surface of Ru-Cr-Mn/Al₂O₃ catalysts and their adsorption and catalytic properties during CO hydrogenation showed interaction between system components and substrate, forming a disordered structure. The nature of the structure depended on the behaviour of adsorbed oxides of C and H, and determines the activity and selectivity of the catalysts.

Hydrogen and CO Intrapellet Diffusion Effects in Ruthenium-Catalyzed Hydrocarbon Synthesis

R. J. MADON and E. IGLESIA, *J. Catal.*, 1994, **149**, (2), 428-437

Intrapellet H₂ and CO concentration gradients within Ru-based catalyst pellets during Fischer-Tropsch (FT) synthesis lead to lighter and more paraffinic hydrocarbon products than when intrapellet diffusion limitations are negligible. Extreme intrapellet diffusion restrictions totally deplete CO near the pellet centre and restore the hydrogenolysis activity of Ru which is usually strongly inhibited by CO during FT synthesis. In the absence of CO, large hydrocarbons that are removed slowly from liquid-filled catalyst pores undergo extensive hydrogenolysis on Ru sites close to the centre of the pellets, leading to lower wax yields and to higher methane and light paraffin selectivity.

HOMOGENEOUS CATALYSIS

Palladium-Catalyzed Syntheses of 2-Arylbenzothiazoles

R. J. PERRY and B. D. WILSON, *Organometallics*, 1994, **13**, (8), 3346-3350

A new synthetic route for the preparation of 2-arylbenzothiazoles is described consisting of the reaction of a haloaromatic compound with an *o*-aminothiophenol in the presence of 95 psig of CO, a Pd catalyst, such as PdCl₂(PPh₃)₂, and 2,6-lutidine in *N,N*-dimethylacetamide. Good yields of products can be obtained through the proper choice of base, which suppresses unwanted amide thioester as well as benzamide and 2-methylbenzothiazole formation. This method is tolerant of a variety of functional groups and offers a route to 2-arylbenzothiazoles complementary to those that normally employ acid chlorides.

Synthesis of Novel Mono- and Diaryl-Substituted [2.2]Paracyclophanes

V. I. ROZENBERG, E. V. SERGEEVA, V. G. KHARITONOV, N. V. VORONTSOVA, E. V. VORONTSOV and V. V. MIKUL'SHINA, *Izv. Akad. Nauk Rossi, Ser. Khim.*, 1994, (6), 1081-1085

Studies of the activity of various Pd and Ni complexes during the cross-coupling reaction of 4-bromo-[2.2]paracyclophane with *p*-tolyl Mg bromide showed that [1,1'-bis(diphenylphosphinoferrocene)]palladium dichloride (PdCl₂.dppf) catalyst was most active for this reaction. A series of new mono- and diaryl [2.2]paracyclophane derivatives with various substituents in the arene ring were prepared with this PdCl₂.dppf catalyst. It is concluded that the cross-coupling of organozinc [2.2]paracyclophane derivatives with aromatic bromides could occur. The composition and structure of the compounds were established. Some correlations between the structure and spectral parameters of mono- and diaryl-substituted [2.2]paracyclophanes were discovered.

Hydrogenation of Heptene-1 in the Presence of Palladium(II) Complexes with Cyclic Aminomethyl Phosphines

R. Z. KHAIRULLINA, A. A. KARASIK and E. YU. MUSAKOVA, *Neftekhimiya*, 1994, **34**, (4), 332-335

Studies of the liquid-phase hydrogenation of heptene-1 by the Pd(II) complex with 1,5,3,7-diazadiphosphocyclooctane and 1,3,5-diazaphosphorinane in a mixture of ethanol and benzole are reported. The results showed the dependence of the activity and selectivity of the reaction on the substitutes for N atoms in the complex, and on the chosen solvents.

New Access to Conjugated Dien- and Enamides. Synthesis of Dehydropipernonaline, Pipernonaline and Related Biologically Active Amides

H. KAGA, Z. AHMED, K. GOTOH and K. ORITO, *Synlett*, 1994, (8), 607-608

An efficient one-pot method for the synthesis of conjugated dien- and enamides by the Pd-catalyzed coupling reaction of (*E*)- β -bromoacrylamides, using Pd(OAc)₂/PPh₃/Na₂CO₃ or PdCl₂(dppf)/K₂CO₃ catalysts, with alkenyl- and alkylboronates is reported. This route provide some biologically active, naturally occurring unsaturated amides, and is the first synthesis of dehydropipernonaline and pipernonaline.

Oxidation of Methanol Catalysed with Giant Palladium Clusters

YA. V. LASTOVYAK, S. L. GLADII, P. I. PASICHNYK, M. K. STARCHEVSKII, YU. A. PAZDERSKII, M. N. VARGAFNIK and I. I. MOISEEV, *Kinet. Katal.*, 1994, **35**, (4), 559-562

Studies of the kinetics of MeOH oxidation by O₂ in the presence of giant Pd clusters of formula Pd₅₀₁Phen₅₀₁(OAc)₁₈₀ showed that the rate of formation of metal formate is proportional to cluster and MeOH concentrations. The kinetic data and the value of the kinetic isotopic effect agreed with the reaction mechanism. The presence of the C-H bond in the coordinated MeOH cluster limits the reaction.

Rhodium Complex Catalyzed Hydroformylation Reactions of Linear and Cyclic Mono- and Diolefins

A. M. TRZECIAK and J. J. ZIÓLKOWSKI, *J. Organomet. Chem.*, 1994, 479, 213–216

The hydroformylation of cyclopentene, cyclohexene, 4-vinylcyclohexene, cycloheptene and cyclooctene was performed by $\text{Rh}(\text{acac})\{\text{P}(\text{O}Ph)_2\}_2/\text{P}(\text{O}Ph)_2$ (I) catalyst at 80°C and 10 atm ($\text{CO} + \text{H}_2$). Only cyclopentene and 4-vinylcyclohexene were hydroformylated at 1 atm and 40°C. The hydroformylation of some cyclic dienes at 10 atm and 80°C was studied by system (I) and by $\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)/\text{PPh}_3$. The main reaction products of cyclohexadienes and pentadiene were unsaturated monoaldehydes.

Regioselective Hydroformylation of Alkenes Catalyzed by Di(*n*-carboxylato)rhodium(I) Complexes

M. P. DOYLE, M. S. SHANKLIN and M. V. ZLOKAZOV, *Synlett*, 1994, (8), 615–616

Hydroformylation of substituted styrenes, 3,3-dimethyl-1-butene and vinyl acetate, catalysed by $[\text{Rh}(\text{cod})(\text{OOCR})_2]$ (cod = 1,5-cyclooctadiene) in the absence of phosphine or phosphite ligands, occurred at 25°C giving high yield and regioselectivities of > 95:5 for branched:linear aldehydes from styrenes and vinyl acetate. An important feature of this Rh pre-catalyst is its exceptional selectivity for monosubstituted alkenes relative to disubstituted alkenes, such as dihydropyran, indene, etc., which are completely unreactive under the hydroformylation conditions. Only the linear aldehyde was obtained with 3,3-dimethyl-1-butene.

Catalysis of Phosphine-Coordinated Rhodium(I) Complexes for 2-Propanol Dehydrogenation

T. MATSUBARA and Y. SAITO, *J. Mol. Catal.*, 1994, 92, (1), 1–8

The Wilkinson complex $\text{RhCl}(\text{PPh}_3)_3$, which is usually inactive for 2-propanol dehydrogenation (1), showed catalytic activity on addition of Et_3N or by using a hydride complex, instead of chloride. This also worked for ketone hydrogenation (2). $\text{RhH}(\text{PPh}_3)_3$ complex exhibited catalytic activity for both (1) and (2). Dissociative and rate-determining dihydrogen evolution steps are proposed.

Isomerization Mechanism of Dinuclear Chloro-Bridged Rhodium(I) Complexes

G. GIORDANO and E. ROTONDO, *Polyhedron*, 1994, 13, (17), 2507–2511

Room temperature studies of the *cis*- and *trans*-halide-bridged dimers $[\{\text{Rh}(\text{CO})(\text{PPh}_3)(\mu\text{-Cl})\}_2]$ showed a rather fast equilibrium of interconversion. NMR shows no Rh–P or Rh–C bond cleavage. This suggests that the equilibrium occurs through dissociation of the dinuclear Rh^I species into the trico-ordinated 14-electron T-shaped $[\text{Rh}(\text{CO})(\text{PPh}_3)\text{Cl}]$ (1). The rate of the isomerisation is accelerated by the presence of small amounts of *cis*- $[\text{Rh}(\text{CO})_2(\text{PPh}_3)(\mu\text{-Cl})]$, which is a precursor of the trico-ordinated fragment (1).

Oxidation of Octyl- α -D-glucopyranoside, Catalysed by $[\text{Ru}(\text{azpy})_2(\text{H}_2\text{O})(\text{py})]^{2+}$ or $[\text{Ru}(\text{azpy})_2(\text{H}_2\text{O})_2]^{2+}$ (azpy = 2-(phenyl)-azopyridine), Produces Octyl- α -D-glucuronic Acid

A. E. M. BOELRIJK and J. REEDIJK, *Recl. Trav. Chim. Pays-Bas*, 1994, 113, (9), 411–412

Highly stable Ru-2-(phenyl)azopyridine catalysts which effect an oxidation of octyl- α -D-glucopyranoside in aqueous conditions with NaBrO_3 as a co-oxidant were developed. The oxidation processes involve a two-electron transfer step: a primary alcohol oxidation and an oxidative hydrolysis mechanism which forms products without the octyl chain. The reactivity and selectivity of both catalytic systems are pH dependent.

FUEL CELLS

Activity and Stability of Ordered and Disordered Co-Pt Alloys for Phosphoric Acid Fuel Cells

M. WATANABE, K. TSURUMI, T. MIZUKAMI, T. NAKAMURA and P. STONEHART, *J. Electrochem. Soc.*, 1994, 141, (10), 2659–2668

Both ordered and disordered Co-Pt alloys, prepared by heat treatment or annealing, respectively, were studied using the well-defined crystallographic structures of the alloy catalysts used for PAFC. The ordered alloy had specific activity 1.35 times higher before corrosion testing than the disordered alloy, but was 0.73 times less active after corrosion tests at 0.8 V and 205°C in 105% H_3PO_4 . The total Pt content did not change in the catalysts even after 50 h of corrosion. The disordered alloy is preferable to the ordered one.

2% Platinum- H_2WO_4 Based Electrocatalysts for Phosphoric Acid Fuel-Cell Cathode

O. SAVADOGO and A. ESSALIK, *J. Electrochem. Soc.*, 1994, 141, (8), L92–L94

A Pt- H_2WO_4 based electrocatalyst, for use as an O cathode in 99% phosphoric acid at 180°C, has been produced inexpensively. For a 2% Pt- H_2WO_4 electrode, the electrocatalytic properties for O reduction, and specific and mass activities were higher than those for 10% Pt. The improvement for a 2% Pt-1% H_2WO_4 may be due to electronic interactions and synergistic effects between electrocatalyst and support.

CORROSION PROTECTION

The Effects of Differing Degrees of Thermal Activation of $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ on Its Corrodability and Oxygen Catalytic Activity

D. WORSLEY and A. MILLS, *J. Mol. Catal.*, 1994, 94, (1), 71–84

The kinetics of dissolution and O catalysis of $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ were studied at ambient to 100°C. Increasing the activation temperature caused an increasingly thick, dissolution-inert and diffuse layer to form on the outside of the particles. There appears to be a link between the H_2O content of hydrated RuO_2 and its activity as an O₂ catalyst.

CHEMICAL TECHNOLOGY

Methane Steam Reforming in Asymmetric Pd- and Pd-Ag/Porous SS Membrane Reactors

J. SHU, B. P. A. GRANDJEAN and S. KALIAGUINE, *Appl. Catal. A, Gen.*, 1994, **119**, (2), 305–325
Electrolessly deposited Pd- and Pd-Ag/porous stainless steel (SS) composite membranes were used to steam reform CH₄ using a Ni/Al₂O₃ catalyst. The CH₄ conversion was greatly enhanced by partial removal of H from the reaction location by diffusion through the Pd-based membranes. At a pressure of 136 kPa, 500°C and a molar steam : CH₄ ratio of 3 with continuous pumping on the permeating side, a CH₄ conversion twice as high as the conversion in a non-membrane system was reached by the Pd/SS membrane.

ELECTRICAL AND ELECTRONIC ENGINEERING

Electronic Conduction Processes in Pt-Doped Tin Oxide Thin Films Prepared by RF Magnetron Sputtering

A. K. HASSAN, R. D. GOULD, A. G. KEELING and E. W. WILLIAMS, *J. Mater. Electron.*, 1994, **5**, (5), 310–314
DC and AC conduction measurements were performed at atmospheric pressure and under vacuum on Pt-doped SnO₂ thin films prepared by RF magnetron sputtering. DC conduction at ~ 1 V was due to Poole-Frenkel excitation of electrons from donor-like impurities. At higher voltages space-charge-limited conductivity was observed. AC conduction showed an increase with angular frequency, ω , of the form ω^s , where $s < 1$, and was identified with hopping between localised states in the amorphous films.

Ohmic Contact Formation in Palladium-Based Metallizations to *n*-Type InP

P. JIAN, D. G. IVEY, R. BRUCE and G. KNIGHT, *J. Electron. Mater.*, 1994, **23**, (9), 953–962
Two Pd-based metallisations Au/Ge/Pd (1) and Pd/Ge (2) contacts to *n*-type InP have been studied. Ohmic contacts were obtained with minimum specific resistances of $2.5 \times 10^{-6} \Omega\text{cm}^2$ and $4.2 \times 10^{-6} \Omega\text{cm}^2$ for (1) and (2), respectively. The annealing regime for ohmic contact formation is 300–375°C for the Au/Ge/Pd/InP and 350–450°C for the Pd/Ge/InP system. Pd reacts with InP giving good metallisation adhesion and contact morphology.

Pd/Zn/Pd/Au Ohmic Contacts to *p*-Type In_{0.47}Ga_{0.53}As/InP

P. W. LEECH, G. K. REEVES and M. H. KIBEL, *J. Appl. Phys.*, 1994, **76**, (8), 4713–4717
Optimum conditions for the fabrication of Pd/Zn/Pd/Au contacts to *p*-type In_{0.47}Ga_{0.53}As/InP were established. The value of the specific contact resistance for the as-deposited contacts was reduced to $\rho_c = 1.2 \times 10^{-5} \Omega\text{cm}^2$ with increasing thickness of the interfacial Zn and Pd layers to 300 Å. Annealing of all of the contact configurations except the Zn = 0 and 20 Å structures produced a reduction in ρ_c to a minimum value of $7.5 \times 10^{-6} \Omega\text{cm}^2$ at 500°C.

Reactive Ion Etching of PbZr_{1-x}Ti_xO₃ and RuO₂ Films by Environmentally Safe Gases

W. PAN, S. B. DESU, I. K. YOO and D. P. VIJAY, *J. Mater. Res.*, 1994, **9**, (11), 2976–2980
Reactive ion etching (RIE) of both PbZr_{1-x}Ti_xO₃ (PZT) thin films and RuO₂ electrodes was performed, using etching gases with low ozone depletion potential and global warming potential. The etching characteristics for both PZT and RuO₂ films are reported as a function of etching time, discharge power density, chamber pressure and additive gas. Etch rates were 250–650 Å/min and 100–400 Å/min for PZT and RuO₂, respectively. An optimised etching condition was obtained for the RIE of ferroelectric capacitors. Etched surfaces showed smooth morphologies.

TEMPERATURE MEASUREMENT

Design of Platinum Resistance Thermometer with Small Magnetic Field Correction

K. NARA, H. KATO and M. OKAJI, *Cryogenics*, 1994, **34**, (12), 1007–1010
A new design for the Pt resistance thermometer has been developed to reduce its magnetic field induced errors. A reduction in the magnetoresistance is obtained by combining four sensor elements together to allow their magnetoresistances to cancel each other. The performance of prototype sensors was studied at 16–140 K under magnetic fields of ≤ 8 T. The optimum result showed a reduction in the magnetic field induced error by a factor of 20 at 19 K. The thermometer can be used in varying magnetic fields, etc.

Immersion Characteristics and Reproducibility of the Gold/Palladium Thermocouple

Y.-G. KIM, K. S. GAM and K. H. KANG, *Metrologia*, 1994, **31**, (2), 145–147
A new Au/Pd thermocouple, studied at the Al and Ag freezing point cells, showed generation of a high thermal emf, reproducibility of $\pm 0.2 \mu\text{V}$ at 961.78°C, excellent immersion characteristics and high sensitivity. The Au/Pd thermocouple has very stable and reproducible thermoelectric properties and could thus be used as a precise secondary reference thermometer in industrial applications at the maximum 50 mK level of uncertainty for the range 0–1000°C.

MEDICAL USES

Aquation of the Anticancer Complex *trans*-[RuCl₂(Him)₂] (Him = imidazole)

O. M. NI DHUBHGHAILL, W. R. HAGEN, B. K. KEPPLER, K.-G. LIPPONER and P. J. SADLER, *J. Chem. Soc., Dalton Trans.*, 1994, (22), 3305–3310
Aquation of the anticancer complex *trans*-[H₂im][RuCl₂(Him)₂] was studied in D₂O at pH 2.4–10 by the observation of paramagnetically shifted ¹H NMR resonances. The complex readily undergoes aquation in aqueous solution with a half-life of 3.4 h at 310 K, a time-scale similar to that for aquation of the Pt drug cisplatin. The three detected products were assigned as mono- and di-aqua species. The rate was similar at low pH, but differed at high pH.