ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Diffusion Coefficients of Deuterium in Palladium Deuteride during Ab- and Desorption in High Pressures of Gaseous Deuterium at 298 K

B. BARANOWSKI and S. M. FILIPEK, *Pol. J. Chem.*, 2001, 75, (7), 1051–1058

Pressure jumps of several kbar in gaseous deuterium (D) at 5–28 kbar, surrounding a PdD wire, were used to measure the diffusion coefficients of D in the solid phase by following changes in the electrical resistance with time. Absorption of D is characterised by a smaller diffusion coefficient than is desorption. Both parameters decrease in value as D pressure increases.

Magnetic and Magneto-transport Properties of $RuSr_2GdCu_2O_8$

I. MATSUBARA, N. KIDA and R. FUNAHASHI, J. Phys.: Condens. Matter, 2001, 13, (24), 5645-5652

The magnetic and magnetotransport properties of non-superconducting RuSr₂GdCu₂O₈ (Ru-1212) were investigated. The Ru sublattice shows a magnetic ordering at magnetic ordering temperature, $T_c = 148$ K. An antiferromagnetic ordering of the Gd sublattice occurs at 2.8 K. The ρ -T behaviour is semiconducting with a kink in the vicinity of the T_c due to the reduction of spin scattering. The negative magnetoresistance is relatively large, $\sim 4\%$ at H = 4 T.

CHEMICAL COMPOUNDS

Preparation and Characterization of Palladium and Platinum Complexes Bearing

1,8-Bis[(diphenylphosphino)methyl]naphthalene

Y. YAMAMOTO, Y. FUKUI, K. MATSUBARA, H. TAKESHIMA, F. MIYAUCHI, T. TANASE and G. YAMAMOTO, J. Chem. Soc., Dalton Trans., 2001, (11), 1773–1781

Reaction of MCl₂(cod) (M = Pt, Pd) with the title compound, (1,8-dpmn), gave MCl₂(1,8-dpmn), as confirmed by X-ray analyses. [M₂(RNC)₆](PF₆)₂ (R = xylyl, 2,4,6-Me₃C₆H₂) formed [M₂(1,8-dpmn)-(RNC)₄](PF₆)₂ or [M₂(1,8-dpmn)₂(RNC)₂](PF₆)₂ depending on the molar ratio.

A Simple Access to Palladium Complexes of Functionalized Heterocyclic Carbenes

H. GLAS, E. HERDTWECK, M. SPIEGLER, A.-K. PLEIER and W. R. THIEL, J. Organomet. Chem., 2001, 626, (1–2), 100–105

Imidazolium iodides, prepared by methylation (using CH₃I) of 2-(1-imidazolyl)cyclohexanol and of an acylated derivative, were reacted with Pd(OAc)₂. The reaction yielded *trans*-I₂PdI₂ complexes bearing functionalised heterocyclic carbene ligands. The complexes were characterised both spectroscopically and by X-ray structure analysis.

Direct Functionalisation of σ -Aryl Ligands: Preparation of Homoleptic Functionalised Aryls of Osmium(IV)

M.-K. LAU, Q.-F. ZHANG, J. L. C. CHIM, W.-T. WONG and W.-H. LEUNG, *Chem. Commun.*, 2001, (16), 1478–1479

 $[Os(C_8H_9)_4]$ (1) $(C_8H_9=2,5$ -dimethylphenyl) was synthesised by alkylation of $[OsO_4]$ with C_8H_9MgBr in diethyl ether. (1) was reacted with pyridinium tribromide (in the presence of Fe powder) to give $[Os(C_8H_8Br)_4]$, which undergoes Suzuki coupling with arylboronic acids to afford a wide range of homoleptic functionalised aryls of Os(IV).

Cp*Ru-Allylcarbene Complexes by Nucleophilic Attack of Cyclic Cp*Ru-Dicarbenes

C. ERNST, O. WALTER and E. DINJUS, J. Organomet. Chem., 2001, 627, (2), 249–254

Reaction of phenylacetylene and its derivatives with Cp*Ru(COD)Cl produced neutral 2,5-bis-substituted dicarbene ruthenacycles chloro-Cp*ruthenacyclopenta-1,3,5-trienes. Nucleophilic attack of PMe₃ or P(OMe)₃ occurs at one α-atom of the ruthenacyclopentatrienes and leads under Ru-Cl bond cleavage to the corresponding Cp*Ru-allylcarbene complexes.

PHOTOCONVERSION

Complete Oxidation of Benzene in Gas Phase by Platinized Titania Photocatalysts

H. EINAGA, S. FUTAMURA and T. IBUSUKI, Environ. Sci. Technol., 2001, 35, (9), 1880–1884

Photocatalytic oxidation of benzene in the gas phase was performed in a flow reactor at room temperature. In a humidified airstream, benzene was quantitatively decomposed to CO₂ over UV-irradiated 1.0 wt.% Pt/TiO₂. As the amount of Pt loaded on the TiO₂ was increased, the rate of CO photooxidation increased. Benzene is first decomposed to CO₂ and CO with selectivities of 94% and 6%, respectively; the CO is subsequently oxidised to CO₂.

Photoinduced Hydrogen Evolution with Cytochrome c_3 -Viologen-Ruthenium(II) Triad Complex and Hydrogenase

N. ASAKURA, T. HIRAISHI, T. KAMACHI and I. OKURA, *J. Mol. Catal. A: Chem.*, 2001, 172, (1–2), 1–7

The cytochrome e_3 -viologen-Ru(II) triad complex, (1), was prepared and characterised. Effective quenching of the photoexcited state of the Ru complex moiety by the bound viologen was observed. When a system containing (1) and hydrogenase is irradiated by visible light, photoinduced H_2 evolution was observed, showing the effective two-step electron transfer from the photoexcited state of the Ru complex moiety to cytochrome e_3 via the bound viologen.

Enhancement of an Anodic Photocurrent for Polymer Langmuir–Blodgett Monolayer Containing Tris(2,2'-bipyridine)ruthenium Complex by Surface Plasmon Excitation

N. FUKUDA, M. MITSUISHI, A. AOKI and T. MIYASHITA, Chem. Lett. Jpn., 2001, (5), 378–379

An anodic photocurrent occurring due to photoinduced electron transfer between excited Ru(bpy)₃²⁺ in a LB film and triethanolamine in an electrolyte solution was greatly enhanced on irradiation by blue light reaching a maximum for an angle of incidence of 71° via surface plasmon resonance, compared to irradiation by transmitted light. The amphiphilic N-dodecylacrylamide copolymer LB film containing Ru(bpy)₃²⁺ was on a Ag electrode.

An Organic Red-Emitting Diode with a Water-Soluble DNA-Polyaniline Complex Containing Ru(boy)₃²*

N. KOBAYASHI, S. UEMURA, K. KUSABUKA, T. NAKAHIRA and H. TAKAHASHI, *J. Mater. Chem.*, 2001, 11, (7), 1766–1768

A Ru(bpy)₃²⁺-based red-emitting diode with a fast turn-on luminance response was fabricated from a novel processable and H₂O-soluble DNA-photopolymerised polyaniline complex containing Ru(bpy)₃²⁺. The device showed a maximum luminance of 1500 cd m⁻² at 11 V. The emission mechanism is not thought to be electrochemical.

ELECTRODEPOSITION AND SURFACE COATINGS

Mechanism of Hydrogen Desorption during Palladium Brush-Plating

R. P. YANG, X. CAI and Q. L. CHEN, Surf. Coat. Technol., 2001, 141, (2-3), 283-285

Continuous and pore-free Pd deposits on Cu were fabricated by brush-plating. The brush-plated Pd was made up of nanoclusters. The anode movement had the function of promoting H₂ bubble release (passive release) during the brush-plating when the sliding speed is high (2 m min⁻¹). During the intermission in the Pd brush-plating process, H₂ bubbles actively escape from the Pd deposit.

Reactive Deposition of Metal Thin Films within Porous Supports from Supercritical Fluids

N. E. FERNANDES, S. M. FISHER, J. C. POSHUSTA, D. G. VLACHOS, M. TSAPATSIS and J. J. WATKINS, *Chem. Mater.*, 2001, 13, (6), 2023–2031

A method for deposition of continuous Pd films (2–80 μ m thick) at controlled depths (80–600 μ m) in porous Al₂O₃ disks is described. Using an opposing reactants chemical fluid deposition technique, H₂ was used to reduce a Pd precursor dissolved in sc-CO₂ at 60°C. The precursor was π -2-methylallyl(cyclopentadienyl)Pd(II) or Pd(II) hexafluoroacetylacetonate. Film position was controlled by adjusting the relative concentrations of H₂ and precursor on opposite sides of the Al₂O₃ substrate.

APPARATUS AND TECHNIQUE

An Amperometric NO₂ Gas Sensor Based on Pt/Nafion® Electrode

K.-C. HO and W.-T. HUNG, Sens. Actuators B, Chem., 2001, 79, (1), 11-16

The title NO_2 sensor was prepared using an impregnation-reduction chemical plating method. The Pt/Nafion® electrode was used as an anode maintained at fixed potential. The sensor was stable for > 27 days and its sensitivity to NO_2 concentrations (0–100 ppm) was 0.16 μ A/ppm. The response time was 45 s and recovery time was 54 s, when step changes in NO_2 concentrations of 0–485 ppm and 485–0 ppm, respectively, were applied.

Some New Insights into the Sensing Mechanism of Palladium Promoted Tin (IV) Oxide Sensor

S. C. TSANG, C. D. A. BULPITT, P. C. H. MITCHELL and A. J. RAMIREZ-CUESTA, J. Phys. Chem. B, 2001, 105, (24), 5737-5742

Switching experiments, temperature programmed reduction and in situ neutron scattering-conductivity were used to investigate the sensing mechanism of 1% Pd/SnO₂ toward H₂-containing gas mixtures. A reversible migration of hydrogenic species from and to the Pd and the underlying Sn oxide surface was obtained (reversible H spillover). A dramatic change in electrical conductivity of the Pd doped SnO₂ material occurs due to the creation or destruction of negatively charged adsorbed O species on the sensor surface. The spillover H species can behave like a shallow donor to the semiconductor oxide.

Disposable Amperometric Glucose Sensor Electrode with Enzyme-Immobilized Nitrocellulose Strip

G. CUI, J. H. YOO, B. W. WOO, S. S. KIM, G. S. CHA and H. NAM, *Talanta*, 2001, **54**, (6), 1105–1111

The electrochemical properties of screen printed C paste electrodes carrying a nitrocellulose strip of known dimensions and pore size, impregnated with glucose oxidase and [Ru(NH₃)₆]³⁺, were studied. The [Ru(NH₃)₆]³⁺ mediator substantially lowered the applied potential (0.0 V vs. Ag/AgCl) for glucose determination and eliminated interference from other oxidisable species. The sensor-to-sensor reproducibility and accuracy of determination were improved.

Magnetoresistance of RuO₂-Based Resistance Thermometers Below 0.3 K

M. WATANABE, M. MORISHITA and Y. OOTUKA, *Cryogenics*, 2001, 41, (3), 143–148

The magnetoresistance of RuO₂-based resistors at 0.05–0.3 K in magnetic fields up to 8 T have been determined. The magnetoresistance is negative at \sim 0.5 T and then becomes positive at larger fields. The magnitude of the negative magnetoresistance increases rapidly as the temperature is lowered, while that of the positive magnetoresistance has smaller temperature dependence. The resistors can be used as thermometers down to at least 15 mK.

HETEROGENEOUS CATALYSIS

Effects of the Proton Content of ZSM-5 and the Amount of Pt on the Hydrodesulfurization Activity of Pt/ZSM-5

T. KUROSAKA, M. SUGIOKA and H. MATSUHASHI, Bull. Chem. Soc. Jpn., 2001, 74, (4), 757–763

The thiophene hydrodesulfurisation (HDS) activity of Pt/ZMS-5 (1) was studied and found to increase as the Pt loading increased. The formation of aromatics was inhibited as Pt loading increased, but the cracking of products was not inhibited by the Pt loading. The proton-exchange ratio of ZSM-5 affected the HDS activity of thiophene over (1). High HDS activity > 6.00 µmol g-cat⁻¹ s⁻¹ was obtained by 5 wt.% Pt on a 50% cation exchanged ZSM-5 support.

Reductive C-Alkylation of Barbituric Acid Derivatives with Carbonyl Compounds in the Presence of Platinum and Palladium Catalysts

B. S. JURSIC and D. M. NEUMANN, Tetrabedron Lett., 2001, 42, (25), 4103-4107

Synthetic procedures have been demonstrated for the preparation of mono- and di-C-alkylated barbituric acid derivatives. Pt and Pd catalysts were used to hydrogenate solutions of unsubstituted, N-mono- and N,N'-disubstituted barbituric acids, and aliphatic and aromatic aldehydes and ketones. The best catalysts were 5 wt.% (dry basis) Pt or Pd, on active C with H₂O content normally 50%.

Selective Hydrogenation of Sunflower Seed Oil in a Three-Phase Catalytic Membrane Reactor

J. W. VELDSINK, J. Am. Oil Chem. Soc., 2001, 78, (5), 443–446 Hydrogenation of sunflower seed oil was carried out in a novel three-phase membrane reactor consisting of a membrane impregnated with Pd. This provided a catalytic interface between the H_2 and the oil. Membranes of α -Al $_2$ O $_3$ with pore sizes of 5 and 20 nm were used. The 5 nm membranes had an Al_2 O $_3$ top layer, while the 20 nm membranes had a ZrO $_2$ layer. Hydrogenations under kinetically controlled conditions showed that oleic and elaidic acid were not hydrogenated in the presence of linoleic acid. High selectivities gave high trans levels.

The Effect of pH and Metal Loading on the Properties of Sol-Gel Rh/SiO₂

C. K. LAMBERT and R. D. GONZALEZ, J. Solid State Chem., 2001, 158, (2), 154–161

The effect of pH and metal loading (0.5–1.5 wt.%) was investigated on the properties of Rh/SiO₂ catalyst (1) prepared by sol-gel processing. The pH of the sol had the most significant effect on the final SiO₂ support structure. (1), prepared at pH \sim 3, had a high metal dispersion and well-defined pore size distribution. As the Rh loading was increased, the gels became more fully condensed. SiO₂ prepared at a pH of \sim 8 showed a significant increase in the degree of condensation regardless of Rh content.

HOMOGENEOUS CATALYSIS

Generation of Hydrogen Peroxide Directly from H₂ and O₂ Using CO₂ as the Solvent

D. HÂNCU and E. J. BECKMAN, *Green Chem.*, 2001, 3, (2), 80–86

 H_2O_2 could be produced directly from H_2 and O_2 in liquid CO_2 solvent, with CO_2 -soluble Pd(II) or Pd(0) catalysts, such as $[Pd(P(C_6H_5)_3)_2]Cl_2$ or $Pd_2(dba)_3$, although Pd(0) catalysts have more potential. The direct H_2 - O_2 reaction was performed in liquid CO_2 in a high-pressure (170 bar) batch reactor at room temperature. In a typical experiment, the reactor was charged with deionised H_2O , H_2SO_4 , Pd catalyst and NH_4Cl . The H_2O_2 can be recovered from CO_2 without the need for large (and expensive) pressure drops.

Selective Palladium-Catalyzed Aminations on Dichloropyridines

T. H. M. JONCKERS, B. U. W. MAES, G. L. F. LEMIÈRE and R. DOMMISSE, *Tetrahedron*, 2001, 57, (32), 7027–7034

The amination of dichloropyridines was catalysed by Pd(OAc)₂/BINAP, with K₂CO₃ as a base. Mild conditions combined with low catalyst loading resulted in maximum selectivity and excellent base-sensitive functional group tolerance. The use of a large amount of K₂CO₃ was crucial to get the reaction to completion. The use of dioxane as solvent instead of toluene gave increased yield. Pyridines can be functionalised using this synthetic route.

On the Amination of Tetraazafulvalenes

C. KÄPPLINGER and R. BECKERT, Synlett, 2001, (7), 1188–1190 Pd₂(dba)₃/rac-BINAP was used to catalyse the amination of tetraazafulvalenes. Starting from either the tetraalkylated compounds or their vinylogous derivatives, substitution of the aryl bromide by different amines was achieved. Compounds which possess four primary amino groups as well as four hydrazino residues were synthesised by a one-pot, two-step method. Bichromophores could be obtained by the introduction of the phenoxazine system into tetraazafulvalenes.

Unexpected Regioselectivity in the Palladium-Catalyzed Reaction of Silacyclobutanes with Aryl Iodides

Y. TANAKA, A. NISHIGAKI, Y. KIMURA and M. YAMASHITA, Appl. Organomet. Chem., 2001, 15, (8), 667–670

The reaction of aryl iodides with 1,1-diphenylsilacyclobutanes (1) gives two classes of compounds, depending on the Pd catalyst used. In the presence of a catalytic amount of Pd(PPh₃)₄, the reaction yields unexpected ring-opening adducts, 1- and 2-propenyl-(triaryl)silanes, in good yields. However, the PdCl₂(PhCN)₂-catalysed reaction of (1) with aryl halides also gives unexpected products, triarylsilanols, after hydrolysis, in moderate yields. The catalysis involves the reaction of aryl-Pd intermediates with silacyclobutanes along with regioselective aryl-Si bond formation.

On the Stereoselectivity in Bisdihydroxylation of 1.5-Cyclooctadiene with Osmium Tetroxide

K. KAWAZOE, Y. FURUSHO, S. NAKANISHI and T. TAKATA, Synth. Commun., 2001, 31, (14), 2107–2112

In the bisdihydroxylation of 1,5-cyclooctadiene with OsO₄, a stoichiometric amount of OsO₄ yielded a 1:1 mixture of syn- and anti-isomers, while a catalytic amount of OsO₄ only gave the isomer syn-(1R*,2.5*,5R*,6.5*)-cyclooctane-1,2,5,6-tetrol. A co-oxidant of N-methylmorpholine N-oxide was used.

Asymmetric Hydrogenation via Architectural and Functional Molecular Engineering

R. NOYORI, M. KOIZUMI, D. ISHII and T. OHKUMA, *Pure Appl. Chem.*, 2001, 73, (2), 227–232

RuCl₂(phosphine)₂(1,2-diamine) complexes, coupled with an alkaline base, such as KOH, KOC(CH₃)₃ or NaOCH(CH₃)₂, in 2-propanol, can preferentially hydrogenate a C=O function over coexisting conjugated or nonconjugated C=C linkages, a nitro group, halogen atoms and various heterocycles. The use of appropriate chiral diphosphines and diamines achieves rapid asymmetric hydrogenation of various aromatic, heteroaromatic and olefinic ketones.

ELECTRICAL AND ELECTRONIC ENGINEERING

Sintering of Screen-Printed Platinum Thick Films for Electrode Applications

J. B. VÉCHEMBRE and G. R. FOX, *J. Mater. Res.*, 2001, **16**, (4), 922–931

Pt electrodes (6–8 μm thick) were produced on Al₂O₃ substrate by a double-print Pt screen printing process that included a sequential heat treatment at 600 and 1300°C. This improved the final sintered double-print film as the first printed layer acted as a sintering template for the second printed layer. The sintered Pt films have a 95% coverage of the Al₂O₃ surface, 92% density, 0.73 μm average surface roughness, and $16 \times 10^{-5} \Omega$ cm resistivity.

Hydrogen-Robust Submicron IrO_x/Pb(Zr,Ti)O₃/Ir Capacitors for Embedded Ferroelectric Memory

T. SAKODA, T. S. MOISE, S. R. SUMMERFELT, L. COLOMBO, G. XING, S. R. GILBERT, A. L. S. LOKE, S. MA, R. KAVARI, L. A. WILLS and J. AMANO, *Jpn. J. Appl. Phys., Part 1*, 2001, 40, (4B), 2911–2916

Submicron IrO_x/PZT/Ir (PZT = Pb(Zr,Ti)O₃) capacitors (1) were fabricated using a one-mask stack-etch process, integrated with a SiO₂ interlayer dielectric, and contacted with Al metallisation. The aggregate electrical properties of integrated (1) were shown to be nearly independent of individual capacitor areas in the range 10^2 – $0.12 \,\mu\text{m}^2$. In fact, switched polarisation values of > 30 $\,\mu\text{C}$ cm⁻² were obtained for (1) with an individual capacitor area of $0.12 \,\mu\text{m}^2$. Hrobust (1) can be obtained using appropriate diffusion barriers. No degradation in ferroelectric properties of (1) was observed.

Process Window Extension of TiN Diffusion Barrier Using Preoxidation of Ru and RuO_x Film for (Ba.Sr)TiO₃ Dielectric Film

D.S. YOON, K. HONG and J. S. ROH, J. Vac. Sci. Technol. A, 2001, 19, (4), 1730-1736

The effects of thin layers of RuO_x formed on the bottom electrodes of a TiN barrier layer of dielectric film was investigated. The Ru(100 nm)/TiN/p-Si/Si contact system had ohmic behaviour at the forward bias at $\leq 550^{\circ}$ C, whereas the RuO_x(100 nm)/TiN/p-Si/Si contact system showed double Schottky characteristics at 400°C. When the oxidation time was reduced from 3 to 1 min, the electrical properties for a Ru(30 nm)/TiN/p-Si/Si contact system improved. Electrical properties are better without Ru oxidation.

Electrical Properties and Thermodynamic Stability of Sr(Ti_{1-x},Ru_x)O₃ Thin Films Deposited by Inductive-Coupling-Plasma-Induced RF Magnetron Sputtering

R. OHARA, T. SCHIMIZU, K. SANO, M. YOSHIKI and T. KAWAKUBO, *Jpn. J. Appl. Phys., Part 1*, 2001, 40, (3A), 1384–1387

 $Sr(Ti_{1-\infty}Ru_{\infty})O_3$ (STRO) epitaxial thin films were deposited on single crystal $SrTiO_3(100)$ substrates using the title magnetron sputtering technique in the absence of O_2 . The electrical conductivity of STRO films increased with Ru concentration and levels of the Ru 4d state were observed in the band gap of $SrTiO_3$ by XPS analysis. Thermodynamic stability increased with the decrease of Ru concentration. STRO (x < 0.50) was free from degradation under an annealing H_2 atmosphere at $600^{\circ}C$.

MEDICAL USES

Thermodynamic Studies on the Effects of Cisplatin or its Analog Complexes on Actin Polymerization H. ZENG, B. WANG and K. WANG, Thermochim. Acta, 2001, 373, (1), 1–5

Thermodynamics parameters of actin polymerisation in the presence of cisplatin or its analog complexes (*is*-DBDP, *is*-DIDP, *is*-DADP) were obtained from direct heat and viscosity measurements at 310.15 K. The relative viscosity of actin polymer decreased in the presence of the Pt complexes, and showed a Pt concentration dependence.

Mixed Ligand Complexes of Ruthenium(II) Containing α,β -Unsaturated- β -ketoamines and Their Antibacterial Activity

T. D. THANGADURAI and K. NATARAJAN, *Transition Met. Chem.*, 2001, 26, (4–5), 500–504

[RuX(CO)(PPh₃)(B)(LL')] (X = Cl; B = PPh₃, pyridine, piperidine, morpholine; LL' = α , β -unsaturated- β -ketoaminate) were synthesised by reacting [RuHCl-(CO)(PPh₃)(B)] with the appropriate β -ketoamine in a 1:1 molar ratio. [RuCl(CO)(bzac- σ -anz)(PPh₃)(py)] had high inhibiting action towards E-coli and Salmonella typhi.