

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Microstructures and Magnetic Properties of Fe-Pt Permanent Magnets

Y. TANAKA, N. KIMURA, K. HONO, K. YASUDA and T. SAKURAI, *J. Magn. & Magn. Mater.*, 1997, **170**, (3), 289–297

The magnetic properties of Fe-38.5Pt, Fe-39.5Pt and Fe-50.0Pt (at.%) alloys were studied after various heat treatment conditions. The magnetic hardness of the Fe-39.5Pt alloy showed a maximum after annealing for 10 h at 873 K. This alloy had the highest coercivity, and was a fully ordered single phase, γ_1 , composed of small antiphase domains of size ~ 10 nm. The magnetic hardness degraded greatly with the formation of a poly-twinned structure.

Hydrogenation Characteristics of $\text{TiFe}_{1-x}\text{Pd}_x$ ($0.05 \leq x \leq 0.30$) Alloys

I. YAMASHITA, H. TANAKA, H. TAKESHITA, N. KURIYAMA, T. SAKAI and I. UEHARA, *J. Alloys Compd.*, 1997, **253–254**, 238–240

The crystal structure and hydriding behaviour of pseudobinary $\text{TiFe}_{1-x}\text{Pd}_x$ ($0.05 \leq x \leq 0.30$) alloys are reported. Increasing the amount of substituted Pd increased the lattice constant while maintaining the CsCl type crystal structure. Partial substitution by Pd, which has superior catalytic and hydriding properties, effectively lowered the activation temperature of the intermetallic TiFe alloy.

Preserved Interfacial Magnetism and Giant Antiferromagnetic Exchange Coupling in Co/Rh Sandwiches

S. ZOLL, A. DINIA, D. STOEFFLER, M. GESTER, H. A. M. VAN DEN BERG and K. OUNADJELA, *Europhys. Lett.*, 1997, **39**, (3), 323–328

The interlayer coupling in Co/Rh/Co sandwiches prepared by UHV evaporation was studied using magnetisation and transport experiments. The antiferromagnetic coupling strength for thin Rh layers was the largest ever found in magnetic systems, reaching ~ 34 erg cm^2 for a 5 Å thick Rh interlayer. This is 7–8 times larger than previously reported for a Co/Ru system.

A Study of the Al-Ni-Ru Ternary System below 50 at.% Aluminium

I. J. HORNER, L. A. CORNISH and M. J. WITCOMB, *J. Alloys Compd.*, 1997, **256**, 213–220

Studies of the Al-Ni-Ru system showed two ternary invariant reactions, peritectic and eutectic, with a binary eutectic between. The Ru-rich solid solution had greater solubility for Ni (~ 30 at.%) than for Al (~ 9 at.%). The Ni-rich solid solution and the phase based on AlNi_3 extended into the ternary to ~ 14 at.%. The extent of the B2 solidification surface was large.

CHEMICAL COMPOUNDS

Preparation of Pd-Pt Bimetallic Colloids with Controllable Core/Shell Structures

Y. WANG and N. TOSHIMA, *J. Phys. Chem. B*, 1997, **101**, (27), 5301–5306

Nanoscope polymer-protected Pd-Pt bimetallic colloids with controllable core/shell structures have been prepared by a so-called H_2 -sacrificial protective strategy. H_2 was used as reducing agent to produce a thin Pt or Pd shell on the preformed poly(*N*-vinyl-2-pyrrolidone)-protected 1–3 nm Pd or Pt core prepared in ethylene glycol. Pd-core/Pt-shell and Pt-core/Pd-shell structures were confirmed by IR-CO probe results.

Formation of a Pt-Carbonyl Colloid by Reaction of Colloidal Pt with CO

F. A. HENGLEIN, *J. Phys. Chem. B*, 1997, **101**, (31), 5889–5894

The formation of Pt-carbonyls from the reaction of CO on colloidal Pt in aqueous media by the citrate method was investigated. The resultant Pt-carbonyls were aggregates of the Pt-carbonyl family $[\text{Pt}_n(\text{CO})_n]^{2-}$ with $n = 1$ to ~ 10 . The Pt-colloid converted into carbonyls in 80–90% yield, but not if the colloid was pretreated with H_2 . When the Pt-carbonyl was treated with KOH, isolated $[\text{Pt}_n(\text{CO})_{18}]^{2-}$ clusters were observed.

A Novel Type of Amidato Coordination: The Metallocycle Rh-Rh-NH-C(Me)=O

V. YU. KUKUSHKIN, T. NISHIOKA, S. NAKAMURA, I. KINOSHITA and K. ISOBE, *Chem. Lett. Jpn.*, 1997, (2), 189–190

The reaction of $[\text{Rh}_2\text{Cp}^*_2(\mu\text{-CH}_2)_2(\mu\text{-O}_2\text{CO})]$, $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$, with acetonitrile in aqueous solution followed by addition of NPF₆ gave the Rh-Rh complex $[\text{Rh}_2\text{Cp}^*_2(\mu\text{-CH}_2)_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-NHC(=O)Me})][\text{PF}_6]$, which is the first example of an amidato complex where the ligand $[\text{NHC(=O)Me}]$ links the metal-metal site forming a new type of metallocycle. It is also among the first examples of hydrolysis of $\text{N}=\text{CR}$ species in Rh complexes.

Activation of Hydrogen on Iridium(I) Centers in Water: Solvent Effects, pH Effects, and Iridium-Hydride Exchange with D₂O

D. P. PATERNITI, P. J. ROMAN and J. D. ATWOOD, *Organometallics*, 1997, **16**, (15), 3371–3376

The water-soluble Ir complexes *trans*- $\text{Ir}(\text{CO})\text{L}_2\text{X}$ ($\text{X} = \text{Cl}, \text{OH}$; $\text{L} = \text{PPh}_2(m\text{-C}_6\text{H}_4\text{SO}_3\text{K})$ (TPPMS), $\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})_3$ (TPPTS)) were used to examine the range of solvent effects for H_2 activation at an Ir(I) centre and of pH changes on the rate of H_2 addition to an organometallic centre. In H_2O the hydride ligands undergo H/D exchange with D_2O with the rate dependant on the *trans* ligand.

Incorporation of $\text{Ru}_2(\text{O}_2\text{C}(\text{CH}_2)_6\text{CH}_3)_4$ into Extended Chains: Interaction of $\text{Ru}_2(\text{O}_2\text{C}(\text{CH}_2)_6\text{CH}_3)_4$ with Pyrazine, 4-Cyanopyridine, TCNE, and *p*-Benzoquinone

J. L. WESEMANN and M. H. CHISHOLM, *Inorg. Chem.*, 1997, 36, (15), 3258–3267

$\text{Ru}_2(\text{O}_2\text{C}(\text{CH}_2)_6\text{CH}_3)_4$ (1) was reacted with bridging ligands possessing extended-systems in order to form conductive polymers. With pyrazine, the polymer [(1)(pz)]_n was isolated, but 4-cyanopyridine (4-cp) gave only the bis-adduct (1)(4-cp)₂. In both cases π -interactions occurred between the Ru-Ru π^* HOMO and the ligand π orbitals. TCNE and *p*-benzoquinone underwent redox reactions, with the latter giving the desired [1⁺][SQ⁻] which was unstable and readily dissociated to give (1) and *p*-benzoquinone.

Preparation and Characterization of $[\text{HRu}_4(\text{CO})_{12-x}(\text{PPh}_2)_x\text{BH}_2]$ ($x = 1-3$) and the Oxidative Addition of a P-H Bond in $[\text{HRu}_4(\text{CO})_{10}(\text{PPh}_2)_2\text{BH}_2]$

C. E. HOUSECROFT, J. S. HUMPHREY and A. L. RHEINGOLD, *Inorg. Chim. Acta*, 1997, 259, (1-2), 85–90

Mono-, di- and trisubstituted Ru products were prepared by the photolysis of $[\text{HRu}_4(\text{CO})_{12}\text{BH}_2]$ with PPh_2 . The solid state structure of $[\text{HRu}_4(\text{CO})_{10}(\text{PPh}_2)_2\text{BH}_2] \cdot \text{CH}_3\text{NO}_2$ was confirmed and the substitution sites assigned. $[\text{HRu}_4(\text{CO})_{10}(\text{PPh}_2)_2\text{BH}_2]$ heated in cyclohexane undergoes oxidative addition of one P-H bond to form $[\text{H}_2\text{Ru}_4(\text{CO})_6(\text{PPh}_2)_2(\mu\text{-PPh}_2)\text{BH}_2]$.

Mixed Valence Properties of a New Binuclear Complex, $[(\text{edtaH})\text{Ru}^{\text{III}}\text{NCRu}^{\text{II}}(\text{CN})_5]^{4-}$ and Kinetic Studies of the Aqua Substitution Reaction in $\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})^-$ by $\text{Ru}(\text{CN})_6^{4-}$

H. C. BAJAJ and A. DAS, *Polyhedron*, 1997, 16, (21), 3851–3855

The synthesis of an asymmetric mixed valence complex, $\text{K}_4[(\text{edtaH})\text{Ru}^{\text{III}}\text{NCRu}^{\text{II}}(\text{CN})_5] \cdot 2\text{H}_2\text{O}$, by the aqua substitution reaction of $[\text{Ru}(\text{edtaH})\text{H}_2\text{O}]$ with $\text{K}_4\text{Ru}(\text{CN})_6$ is reported. An associative mechanism for the substitution reaction with a second order rate constant of $13.8 \pm 0.6 \text{ M}^{-1}\text{s}^{-1}$ at 25°C and pH = 5.0 was observed. The complex displayed a metal-to-metal charge transfer maximum at 682 nm in H_2O at 25°C.

ELECTROCHEMISTRY

Oxygen Electroreduction on Titanium-Supported Thin Pt Films in Alkaline Solution

K. TAMMEVESKI, M. ARULEPP, T. TENNO, C. FERRATER and J. CLARET, *Electrochim. Acta*, 1997, 42, (19), 2961–2967

The electrochemical reduction of O_2 at thin Pt films on Ti was studied in alkaline solution and the kinetics were shown to be qualitatively the same as at Pt/glassy C electrodes. Tafel plots showed a slope of -60 mV dec^{-1} at low-, and -260 to -490 mV dec^{-1} at high-current densities. The potential of the H_2 adsorption-desorption peaks and the Pt oxide reduction peak shifted towards positive potentials with increasing Pt film thickness in KOH and H_2SO_4 .

Electrocatalytic Hydrogenation of Organic Compounds on a Poly[*N*-(5-hydroxypentyl)pyrrole] Film-Coated Electrode Incorporating Palladium Microparticles

N. TAKANO, A. NAKADE and N. TAKENO, *Bull. Chem. Soc. Jpn.*, 1997, 70, (4), 837–840

A poly[*N*-(5-hydroxypentyl)pyrrole] film-coated C-fibre electrode incorporating Pd metal microparticles was studied for the electrochemical hydrogenation of organic compounds. The electrode showed a high catalytic ability and good physical stability with respect to H_2 evolution, and was effective for the hydrogenation of unsaturated nitro, quinone and carbonyl compounds, giving high yields and current efficiencies. This system also worked for the hydrogenative deprotection of a benzyl group and also for the dehalogenation of bromobenzene.

PHOTOCONVERSION

Photoinduced Hydrogen Evolution by Using Platinum-Loaded Langmuir-Blodgett and Cast Films of Porphyrin

H. HOSONO, *Chem. Lett. Jpn.*, 1997, (10), 523–524

Pt-loaded Langmuir-Blodgett (1) and cast films (2) of a porphyrin have been prepared and steady photoinduced H_2 evolution observed from both films under steady state irradiation. The porphyrin turnover number in (1) and (2) reached 360 and 151, respectively, after 354 h irradiation and the rate of H_2 evolution was roughly twice as high on (2) as on (1).

Characterization of Excited Electronic and Vibronic States of Platinum Metal Compounds with Chelate Ligands by Highly Frequency-Resolved and Time-Resolved Spectra

H. YERSIN, W. HUMBS and J. STRASSER, *Topics Curr. Chem.*, 1997, 191, 153–249

A comprehensive review is given of the lowest excited electronic states of triplet character and related vibronic properties of per-protonated, per-deuterated and partially deuterated $[\text{Pt}(\text{bpy})_2]^{2+}$, $[\text{Rh}(\text{bpy})_2]^{3+}$, $[\text{Ru}(\text{bpy})_2]^{2+}$ and $[\text{Os}(\text{bpy})_2]^{2+}$ based on highly frequency-resolved and time-resolved emission and excitation spectra. Data for other Ru and Pt complexes are given. The role of traps and sites is discussed in the context of high-resolution, site-selective, and line-narrowed spectra of chromophores doped into matrices. It is emphasised that chemical tunability may allow the controlled variation of physical properties. (321 Refs.)

Photochemistry of the IrCl_6^{2-} Complex in Methanol Matrices

E. M. GLEBOV, V. F. PLYUSNIN, V. L. VYAZOVKIN and A. B. VENEDIKTOV, *J. Photochem. Photobiol. A: Chem.*, 1997, 107, (1-3), 93–99

The photochemistry of IrCl_6^{2-} in MeOH matrices frozen at 77 K was studied by ESR. Photoreduction produced IrCl_6^{3-} and a $\cdot\text{CH}_2\text{OH}$ radical which gave rise to the radical complex, $\text{IrCl}_6^{\cdot-} \dots \cdot\text{CH}_2\text{OH}$; this showed a maximum at 287 nm. When the matrix was heated at 115 K, this complex disappeared.

Dynamical Processes in the Lowest-Excited Triplet Metal-to-Ligand Charge Transfer States of Ruthenium and Osmium Diimine Complexes in Crystals

H. RIESEN, L. WALLACE and E. KRAUSZ, *Int. Rev. Phys. Chem.*, 1997, **16**, (3), 291–359

The lowest-excited states in Ru(II) and Os(II) diimine complexes, based on studies of their optical spectra in crystalline environments, are reviewed. The transferred charge in the lowest-excited triplet metal-to-ligand charge transfer states is localised on a single ligand in Ru(II) diimine complexes and the excitation exchange interaction between equivalent metal-ligand subunits is $< 0.5 \text{ cm}^{-1}$. (70 Refs.)

Photocatalytic and Aerobic Oxidation of Saturated Alkanes by a Neutral Luminescent *trans*-dioxoosmium(VI) Complex [OsO₂(CN)₂(dpphen)]

J. Y. K. CHENG, K.-K. CHEUNG, C.-M. CHE and T.-C. LAU, *Chem. Commun.*, 1997, (15), 1443–1444

A neutral *trans*-Os(VI) complex [OsO₂(CN)₂(dpphen)] (dpphen = 4,7-diphenyl-1,10-phenanthroline), which can mediate the photocatalytic oxidation of saturated alkanes in the presence of O₂, was emissive in the solid state and in solution at room temperature with emission occurring at 635 nm with an excited state lifetime of 0.95 μs in MeCN. Under UV-VIS irradiation, cyclohexane was oxidised to cyclohexanol and cyclohexanone with a turnover number of 16.

APPARATUS AND TECHNIQUE

Adsorptive Stripping Measurements of Chromium and Uranium at Iridium-Based Mercury Electrodes

J. WANG, J. WANG, B. TIAN and M. JIANG, *Anal. Chem.*, 1997, **69**, (8), 1657–1661

Ir-based Hg electrodes are used for adsorptive stripping measurements of Cr and U in the presence of the DTPA and propyl gallate complexing agents. Detection limits of $0.4 \mu\text{g l}^{-1}$ U and $0.5 \mu\text{g l}^{-1}$ Cr were obtained after a 10 min adsorptive accumulation. This system is applicable to on-site measurements of trace U and Cr, such as in groundwater and soil samples. The electrodes are highly stable and contain less Hg than standard hanging Hg drop electrodes.

Sol-Gel Based Amperometric Biosensor Incorporating an Osmium Redox Polymer as Mediator for Detection of L-Lactate

T.-M. PARK, E. I. IWUOHA, M. R. SMYTH, R. FREANEY and A. J. MCSHANE, *Talanta*, 1997, **44**, (6), 973–978

A novel amperometric biosensor for the determination of lactate was made by immobilising lactate oxidase and the redox polymer [Os(bpy)₂(PVP)₁₀Cl]Cl onto the surface of a glassy C electrode, followed by coating with a sol-gel film derived from methyltriethoxysilane. Lactate was determined at 400 mV and the range of linear response, slope of linear response and detection limit were 0.1–9 mM, $1.02 \mu\text{A mM}^{-1}$ and 0.05 mM, respectively.

HETEROGENEOUS CATALYSIS

Kinetics and Mechanism of the Reduction of NO by C₃H₈ over Pt/Al₂O₃ under Lean-Burn Conditions

R. BURCH and T. C. WATLING, *J. Catal.*, 1997, **169**, (1), 45–54

The effects of temperature, contact time and reactant concentration on the lean deNO_x reaction over Pt/Al₂O₃, using C₃H₈ as the reductant, were studied and a kinetic model developed. Adsorbed atomic O was the main species on the metal surface, inhibiting C₃H₈ oxidation by O₂ and facilitating the oxidation of NO to NO₂. The reaction rate was determined by dissociative chemisorption of C₃H₈ involving the breaking of a C-H bond. Possible mechanisms for the reduction of NO to N₂ and N₂O are discussed.

Conversion of Canola Oil to Various Hydrocarbons over Pt/HZSM-5 Bifunctional Catalyst

S. P. R. KATIKANENI, J. D. ADJAYE and N. N. BAKHSI, *Can. J. Chem. Eng.*, 1997, **75**, (2), 391–401

The catalytic conversion of canola oil was studied over 0.5 wt. % Pt/HZSM-5 at atmospheric pressure in a fixed bed micro-reactor at 400–500°C. The gas yields were between 22 to 65 wt. % and higher in the presence of steam. The C₄ *iso/n*-alkane ratios were higher, but the organic liquid product (OLP) yields were slightly lower, compared with pure HZSM-5 catalyst. The major components of OLP were aliphatic and aromatic hydrocarbons.

Reforming of Hexane with Pt/Zelite Catalysts

L.-X. DAI, Y. HASHIMOTO, H. TOMINAGA and T. TATSUMI, *Catal. Lett.*, 1997, **45**, (1, 2), 107–112

The aromatisation and isomerisation of *n*-hexane were investigated over various zeolite-supported Pt catalysts. For Pt/K- β , Pt/K-mordenite and Pt/K-L, the addition of KCl increased the selectivity towards benzene formation and decreased selectivity towards hydroisomerisation. The treatment of Pt/K-FSM-16 with K₂CO₃ decreased the formation of cracking products and increased benzene selectivity. Above 623 K, Pt/H-FSM-16 and Pt/H-L catalysts showed lower cracking selectivity and higher isomerisation selectivity than Pt/H- β , with Pt/H-FSM-16 being more resistant to deactivation at high temperatures.

Catalytic Properties of Pt-Ge Intermetallic Compounds in the Hydrogenation of 1,3-Butadiene

T. KOMATSU, S.-I. HYODO and T. YASHIMA, *J. Phys. Chem. B*, 1997, **101**, (28), 5565–5572

The catalytic properties of Pt-Ge intermetallic compounds, Pt₃Ge, Pt₂Ge and PtGe were studied for the H₂-D₂ equilibration and the hydrogenation of 1,3-butadiene. These intermetallic compounds showed lower activity for H₂ dissociation than pure Pt which decreased with decreasing Pt content and resulted in low hydrogenation activity. A high selectivity for butenes resulted from the lower selectivity for butene hydrogenation than 1,3-butadiene hydrogenation.

A Highly Catalytic Bimetallic System for the Low-Temperature Selective Oxidation of Methane and Lower Alkanes with Dioxygen as the Oxidant

M. LIN, T. HOGAN and A. SEN, *J. Am. Chem. Soc.*, 1997, **119**, (26), 6048–6053

A bimetallic system consisting of a mixture of CuCl₂ and metallic Pd in a 3:1 mixture of CF₃CO₂H and H₂O, in O₂ and CO, is highly catalytic for the low temperature selective oxidation of CH₄, C₂H₆ and *n*-butane. CH₄ was selectively converted to MeOH at the rate of $\sim 65 \times 10^{-4}$ M min⁻¹ at 145–150°C. Both C–H and C–C cleavage products were observed for C₂H₆ and *n*-butane giving MeOH, EtOH and acetic acid.

Preparation, Characterisation and Catalytic Hydrogenation Properties of Palladium Supported on C₆₀

R. YU, Q. LIU, K.-L. TAN, G.-Q. XU, S. C. NG, H. S. O. CHAN and T. S. A. HOR, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, (12), 2207–2210

A C₆₀-supported Pd catalyst was prepared by reacting C₆₀ and Pd(OAc)₂(PPh₃)₂ in toluene to give the complex C₆₀[Pd(OAc)₂(PPh₃)₂], which was heated in H₂ at 523 K for 4 h. 1 mol% of the catalyst promoted hydrogenation of diphenylacetylene, phenylacetylene, cyclohexene and hex-1-ene to give 100% conversion to 1,2-diphenylethane, phenylethane, cyclohexane and hexane after 18, 13, 21 and 12 min, respectively. Similar hydrogenations over a Pd/active charcoal catalyst gave similar yields but took longer.

Oxidation of CO and Hydrocarbons on Palladium Zeolite Containing Catalysts

YU. G. EGIAZAROV, *Neftekhimiya*, 1997, **37**, (3), 230–239

The effect of reaction conditions on the physico-chemical properties of a Pd/zeolite catalyst was studied during CO and hydrocarbon oxidation. When ≤ 30 wt.% of zeolite NaY was inserted into the matrix of amorphous aluminosilicate, highly stable zeolite granules were obtained. The optimum dispersion was obtained by depositing 15–30 Å Pd particles on the support by calcination at 300°C followed by reduction in H₂ at 500°C. The activity of the catalyst decreased with the increase in acidity of the support, but the electron-deficiency increased due to adsorption changes.

Effect of Hydrogen Treatment of Active Carbon as a Support for Promoted Ruthenium Catalysts for Ammonia Synthesis

Z. ZHONG and K.-I. AIKA, *Chem. Commun.*, 1997, (13), 1223–1224

The treatment of active C with H₂ at 1073–1188 K for >12 h leads to the elimination of surface impurities such as S, N, O and Cl. This treatment along with pre-reduction of the catalyst, was found to double or triple the activities of Cs⁺-, Ba²⁺- or Ce³⁺-promoted Ru catalysts for NH₃ synthesis. When 2 mass% Ru–BaO/active C (Ba/Ru = 5) was used, the reaction gave 2 mmol NH₃ h⁻¹g⁻¹ at 588 K under 1 atm. The activity increased with prolonged H₂ treatment of the active C.

HOMOGENEOUS CATALYSIS

A Novel Stereoselective and Catalytic C-C Coupling Reaction: Acetylene Dimerization Accompanied by Addition of Iodine to Yield (*E,E*)-1,4-diiodobuta-1,3-diene in the Pt^{IV}-I₂-MeOH System

S. A. MITCHENKO, V. P. ANANIKOV, I. P. BELETSKAYA and Y. A. USTYNYUK, *Mendeleev Commun.*, 1997, (4), 130–131

The dimerisation of acetylene followed by addition of I₂ occurs at 30°C in a MeOH solution of NaI, Na₂PtCl₆·6H₂O and I₂ to yield selectively (*E,E*)-1,4-diiodobuta-1,3-diene in virtually quantitative yield. A proposed mechanism involves the formation, via 2 triple bond iodoplatination steps, of an intermediate *cis*-divinyl Pt(IV) derivative followed by reductive elimination of the product.

Catalytic Colloidal Pd Dispersions in Water-Organic Solutions of Quaternary Ammonium Salt

Y. BERKOVICH and N. GARTI, *Colloids Surf. A: Physicochem. Eng. Aspects*, 1997, **128**, (1–3), 91–99

Colloidal Pd, prepared in H₂O-organic microemulsions containing the cationic surfactant aliquat 336, was found to catalyse the transfer hydrogenolysis of *p*-bromotoluene with Na formate. Catalytic activity increased with a decrease in particle size. The particle size was controlled by the preparation conditions with coarser particles being formed at higher water contents and lower temperatures.

Novel Rhodium-Catalyzed Cyclic Carbonylation of 2-Phenylethynylbenzoates Leading to Indeno[1,2-*c*]isocoumarin

T. SUGIOKA, E. YONEDA, K. ONITSUKA, S.-W. ZHANG and S. TAKAHASHI, *Tetrahedron Lett.*, 1997, **38**, (28), 4989–4992

The carbonylation of ethyl 2-phenylethynylbenzoate under H₂O-gas shift reaction conditions was catalysed by Rh₂(CO)₁₀ in the presence of PPh₃, Et₃N, CO and H₂O in 1,4-dioxane. The tetracyclic lactone, indeno[1,2-*c*]isocoumarin was the major product, derived from bond fission of the ester group and C–H bond activation of the phenyl group.

Liquid-Biphase Hydrogenolysis of Benzo[*b*]thiophene by Rhodium Catalysis

C. BIANCHINI, A. MELI, V. PATINEC, V. SERNAU and F. VIZZA, *J. Am. Chem. Soc.*, 1997, **119**, (21), 4945–4954

The catalytic activity of the zwitterionic complex [(sulphos)Rh(cod)] (sulphos = -O₂S(C₆H₄)CH₂C(CH₂PPh₂)₂) for the hydrogenation and hydrogenolysis of benzo[*b*]thiophene was studied in either MeOH or liquid-biphase systems of MeOH or MeOH–H₂O and *n*-heptane. Under neutral conditions the selective hydrogenation proceeded slowly to give 2,3-dihydrobenzo[*b*]thiophene. In the presence of NaOH selective hydrogenolysis gave the 2-ethylthiophenol Na salt in ~ 5 h. This method can remove residual thiophenic contaminants from petroleum distillates.

Enantioselective Hydrogenation of Imines with Chiral (Phosphanodihydrooxazole)-iridium Catalysts

P. SCHNIDER, G. KOCH, R. PRÉTÔT, G. WANG, F. M. BOHNEN, C. KRÜGER and A. PFALTZ, *Chem. Eur. J.*, 1997, 3, (6), 887–892

Cationic Ir(I) complexes of chiral phosphanodihydrooxazoles were used for the enantioselective hydrogenation of prochiral *N*-alkyl and *N*-aryl imines. For *N*-aryl imines of acetophenone, enantiomeric excesses (ee) of $\approx 79\%$ were obtained. On hydrogenation of the *N*-phenyl imine of acetophenone, up to 89% ee and turnovers numbers approaching 5000 were achieved with 0.1 mol% of catalyst.

Novel Ruthenium-Based Catalyst Systems for the Ring-Opening Metathesis Polymerization of Low-Strain Cyclic Olefins

A. DEMONCEAU, A. W. STUMPF, E. SAIVE and A. F. NOELS, *Macromolecules*, 1997, 30, (11), 3127–3136

Versatile and highly active catalyst systems for the ring-opening metathesis polymerisation of strained and low strain olefins were prepared from RuCl₂(arene)(PR₃)₂ precursors after activation with (trimethylsilyl)diazomethane. Polymerisation of cyclooctene derivatives bearing acetal, ether, ester, epoxide, etc., functionalities gave polymers in good yields.

FUEL CELLS

Electrocatalytic Oxidation of Methanol on Platinum Nanoparticles Electrodeposited onto Porous Carbon Substrates

F. GLOAGUEN, J.-M. LÉGER and C. LAMY, *J. Appl. Electrochem.*, 1997, 27, (9), 1052–1060

In order to enhance catalyst use on MeOH fuel cell electrodes, thin layers of various C powders and recast Nafion[®] were electrochemically plated with Pt. Both the Pt mass and specific activity for MeOH oxidation increased with the amount of surface oxides on the C support. It is concluded that the Pt activity for the MeOH oxidation is not directly related to particle size but to the fine structures of the Pt surface, which may depend on the Pt specific surface area, the nature of the substrate or preparation method of the catalyst.

ELECTRICAL AND ELECTRONIC ENGINEERING

Pd/Zn/Pd Ohmic Contacts to *p*-Type GaP

B. LI, E. LIU and F. ZHANG, *Solid-State Electron.*, 1997, 41, (6), 917–920

Low resistance ohmic contacts to Zn-doped *p*-type GaP were fabricated using an annealed Pd/Zn/Pd metallisation. After heating, the Pd/Zn/Pd multilayer structure had good ohmic characteristics. The quality of the ohmic layer depended on the time and temperature of alloying. When the surface hole concentration of the *p*-type GaP was $2 \times 10^{17} \text{ cm}^{-3}$, a specific contact resistance of $6 \times 10^{-5} \Omega \text{ cm}^2$ was obtained at the optimum alloying temperature of 550°C and time of 3 minutes.

Comparison of Interfacial and Electronic Properties of Annealed Pd/SiC and Pd/SiO₂/SiC Schottky Diode Sensors

L.-Y. CHEN, G. W. HUNTER, P. G. NEUDECK, G. BANSAL, J. B. PETTIT and D. KNIGHT, *J. Vac. Sci. Technol. A*, 1997, 15, (3), 1228–1234

The effects of placing a thin layer of SiO₂ between the Pd and the SiC of Pd/SiC Schottky diodes used as H₂ and hydrocarbon gas sensors were studied. The electrical response and interfacial properties of Pd/SiC (1) and Pd/SiO₂/SiC (2) Schottky diodes were compared after annealing at 425°C for 140 h. The thin SiO₂ layer decreased vertical interdiffusion and Pd/Si formation between the Pd and SiC, and formed a stable sharp (Pd+Pd₂Si)/SiC interface. But, due to the SiO_x layer formation, further stabilisation is needed.

Conductive Powder Preparation and Electrical Properties of RuO₂ Thick Film Resistors

K.-M. YI, K.-W. LEE, K.-W. CHUNG, W.-S. UM, H.-S. LEE, J.-K. SONG and I.-S. LEE, *J. Mater. Sci., Mater. Electron.*, 1997, 8, (4), 247–251

Powder and electrical characteristics of thick film resistors (TFRs) using RuO₂ powders were studied. The resistivity of TFRs decreased and the temperature coefficient of resistance (TCR) became more positive with decreasing crystalline size. TFRs having conductive powders of higher specific surface area at the same crystalline size showed lower resistivity and higher TCR values.

Characterization of a Sol-Gel Derived Pb(Zr, Ti)O₃ Thin-Film Capacitor with Polycrystalline SrRuO₃ Electrodes

K. AOKI, I. MURAYAMA, Y. FUKUDA and A. NISHIMURA, *Jpn. J. Appl. Phys.*, 1997, 36, (6A), L690–L692

Studies of a sol-gel derived Pb(Zr, TiO), thin-film capacitor with polycrystalline top and bottom SrRuO₃ electrodes showed the formation of Pb(Zr, Ti)O₃ columnar grain thin-film with excellent crystallinity on the SrRuO₃ substrate. SrRuO₃/Pb(Zr, Ti)O₃/SrRuO₃ capacitors had good reversibility at an applied voltage of 3.0 V. The remanent polarisation density for 3.0 V was 14.3 $\mu\text{C cm}^{-2}$; degradation was not observed.

MEDICAL USES

Room-Temperature Phosphorescent Palladium-Porphine Probe for DNA Determination

M. ROZA-FERNÁNDEZ, M. J. VALENCIA-GONZÁLEZ and M. E. DÍAZ-GARCÍA, *Anal. Chem.*, 1997, 69, (13), 2406–2410

The room-temperature phosphorescence (RTP) enhancement of a Pd-TMPyP complex (1) (TMPyP = tetrakis(1-methyl-4-pyridyl)porphine) by DNA is reported. When bound to double-stranded DNA the complex (1) showed intense RTP and little reactivity to RNA, which allows the selective quantitative determination of DNA in the presence of RNA. The calibration graphs were linear up to $6 \times 10^{-5} \mu\text{M}$ DNA with a detection limit of $5 \times 10^{-5} \mu\text{M}$.