

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Shape-Selective Preparation and Properties of Oxalate-Stabilized Pt Colloid

X. FU, Y. WANG, N. WU, L. GUI and Y. TANG, *Langmuir*, 2002, 18, (12), 4619–4624

Pt colloids with different shape distributions were prepared by reducing $K_2[Pt(C_2O_4)_2]$ (1), K_2PtCl_4 or K_2PtCl_6 in H_2O with H_2 in the presence of an oxalate stabilising agent. Pt nanoparticles (2) obtained from (1) have quite a narrow size and shape distribution. The addition of $CaCl_2$ or increasing the reaction temperature accelerated the reduction of (1). (2) could connect and fuse into Pt nanowires after exposure in air for a long time, and the process of fusing could be accelerated by H_2 treatment at room temperature.

High-Temperature Ion Source for Elements of Platinum-Palladium Group

A. P. BELOKUROV, R. N. KOUSMINE, M. I. MARTYNOV and D. V. SOKOLOV, *Rev. Sci. Instrum.*, 2002, 73, (2), 748–750

An ion source which is able to work by cw-operation for a long time at the gas-discharge chamber temperature of $\geq 1500^\circ C$ has been developed. Special graphite heaters were employed. The heating method involves combining heat radiation and electronic heating. A Pd ion source with an ion current density $< 60 \text{ mA cm}^{-2}$, which operates in a steady-state condition for $> 100 \text{ h}$, was achieved.

The Isothermal and Isochronal Kinetics of the Crystallisation of Bulk Amorphous $Pd_{40}Cu_{30}P_{20}Ni_{10}$

A. T. W. KEMPEN, F. SOMMER and E. J. MITTEMEIJER, *Acta Mater.*, 2002, 50, (6), 1319–1329

The amorphous alloy $Pd_{40}Cu_{30}P_{20}Ni_{10}$ was obtained by H_2O quenching the molten alloy. By applying appropriate isothermal pre-annealing temperatures, nucleation of the crystalline phases takes place to different extents. The initial state for the subsequent isochronal crystallisation can be changed gradually with respect to the number of pre-existing nuclei. The mode of nucleation changes from site saturation to continuous nucleation during the crystallisation.

CHEMICAL COMPOUNDS

Structural Characterization of the 'Lantern-Shaped' Platinum(III) Complex $[Pt_2Cl_2\{N(H)C(Bu')O\}_4]$

A. DOLMELLA, F. P. INTINI, C. PACIFICO, G. PADOVANO and G. NATILE, *Polyhedron*, 2002, 21, (3), 275–280

A new Pt(III) 'lantern-shaped' complex with amide bridging ligands, $[Pt_2Cl_2\{N(H)C(Bu')O\}_4]$ (1), was synthesised and structurally characterised by XRD. Both (1) and $[Pt_2I_2\{N(H)C(Me)O\}_4]$ exhibit similar very short $N\cdots O$ bite distances. The Pt(III)–Pt(III) distance is significantly shorter in (1).

Synthesis and Reactions of Water-Soluble Diorganoplatinum(II) Complexes

S. KOMIYA, M. IKUINE, N. KOMINE and M. HIRANO, *Chem. Lett. Jpn.*, 2002, (1), 72–73

Ligand displacement reactions of $PtR_2(cod)$ with H_2O soluble 1,2-bis{di(hydroxymethyl)phosphino}-ethane or tris(hydroxymethyl)phosphine gave H_2O soluble PtR_2L_2 ($L_2 = (HOCH_2)_2PCH_2CH_2P(CH_2OH)_2$, $R = Me, Et$ (1), Ph ; $L = P(CH_2OH)_3$, $R = Me, Et$ (2), Ph) at room temperature. Thermolyses of (1) and (2) at $80^\circ C$ liberate ethylene and ethane via β -hydrogen elimination and hydrolysis.

Sr_3NiRhO_6 and Sr_3CuRhO_6 —Two New One-Dimensional Oxides. Magnetic Behavior as a Function of Structure: Commensurate vs Incommensurate

K. E. STITZER, W. H. HENLEY, J. B. CLARIDGE, H.-C. ZUR LOYE and R. C. LAYLAND, *J. Solid State Chem.*, 2002, 164, (2), 220–229

Sr_3NiRhO_6 and Sr_3CuRhO_6 were synthesised in both a commensurate and an incommensurate form. The magnetic susceptibility of Sr_3NiRhO_6 shows an abrupt drop at 30 K, indicative of antiferromagnetic correlations between the chains containing transition metal. Sr_3CuRhO_6 displays ferromagnetic-type ordering below 10 K.

Pairing of Propellers: Dimerization of Octahedral Ruthenium(II) and Osmium(II) Complexes of Eilatin via π - π Stacking Featuring Heterochiral Recognition

D. GUT, A. RUDI, J. KOPILOV, I. GOLDBERG and M. KOL, *J. Am. Chem. Soc.*, 2002, 124, (19), 5449–5456

The dimerisation via π - π stacking of racemic $[M(L-L)_2(\text{eilatin})]^{2+}$ (1) ($M = Os, Ru$; $L-L =$ bipyridyl-type ligands) was studied. The X-ray structures of (1) revealed that they are organised as discrete dimers in which the eilatin residues of each complex are stacked in centrosymmetric packing. The 1H NMR spectra were indicative of fast dimer–monomer equilibrium.

Microwave Accelerated Synthesis of Cyclopentadienyl Bis-phosphine Ruthenium (II) Thiolate Complexes Using Focused Microwave Irradiation

N. KUHNERT and T. N. DANKS, *J. Chem. Res. (S)*, 2002, (2), 66–68

$[RuCp(dppm)SR]$ complexes were obtained from $[RuCp(PPh_3)_2Cl]$ under microwave conditions in yields comparable to the conventional thermal process. The reaction is compatible with functional groups such as esters, carboxylic acids and amides on the thiolato ligands. The reaction times under focused microwave irradiation are cut from 2 h to 2 minutes.

ELECTROCHEMISTRY

A *trans*-Platinum(II) Complex as a Single-Molecule Insulator

M. MAYOR, C. VON HÄNISCH, H. B. WEBER, J. REICHERT and D. BECKMANN, *Angew. Chem. Int. Ed.*, 2002, 41, (7), 1183–1186

Immobilisation of the Pt(II) complex formed from *trans*-bis(triphenylphosphane)PtCl₂ and (4-ethynyl)-phenyl thioacetate between two Au electrodes gives a single molecule insulator. The current/voltage characteristics shows behaviour typical of an insulator, with a tunnel barrier height of 2.5 eV. The complex is anchored to the Au electrodes through the S atoms.

Kinetics of IrCl₆²⁻ Ion Transfer across the Water/1,2-Dichloroethane Interface and the Effect of a Phospholipid Monolayer

J. ZHANG and P. R. UNWIN, *Langmuir*, 2002, 18, (6), 2313–2318

Ion transfer (IT) of IrCl₆²⁻ (1) across a H₂O/1,2-dichloroethane interface was investigated using the techniques microelectrode measurements at expanding droplets and scanning electrochemical microscopy (SECM). (1) transferred across the interface with an apparent transfer coefficient of 0.63 ± 0.05. SECM-double potential step chronoamperometry showed that the system L- α -phosphatidyl ethanolamine, dilauryl significantly diminished the rate of IT, with the retardation effect being dependent on the interfacial phospholipid concentration.

Preparation and Characterisation of Ti/RuO₂ Anodes Obtained by Sol-Gel and Conventional Routes

A. J. TEREZO and E. C. PEREIRA, *Mater. Lett.*, 2002, 53, (4–5), 339–345

Ti/RuO₂ anodes and RuO₂ powders were obtained by the thermal decomposition of RuCl₃ using the 2-propanol solution method (1) and the polymer precursor method (2). SEM showed that the electrode coatings obtained by (2) are rougher than those prepared by (1). XRD found that the crystallite size of the materials by (2) are smaller than those by (1). Higher voltammetric charge and stability in acid medium were exhibited by the electrodes from (2).

PHOTOCONVERSION

Photochemical Formation of Palladium Patterns on Surface-Modified Polyimide Resin

M. SEITA, H. NAWAFUNE, T. NISHIOKA, S. MIZUMOTO and T. KANAI, *J. Appl. Electrochem.*, 2002, 32, (3), 349–352

A simplified method for forming a Pd circuit on a polyimide resin has been demonstrated. A carboxyl group was introduced onto a polyimide resin surface by a KOH treatment and Pd(II) ions were adsorbed by ion exchange. Irradiation by UV of the adsorbed Pd(II) layer treated with a Na formate solution gave a Pd thin film (1). The maximum conductivity of (1) was $9 \times 10^{-3} \text{ S cm}^{-1}$. Pd circuit patterns were formed on the polyimide without a plating resist, by irradiation through a metal-on-quartz lithographic mask.

High-Efficiency Polymer-Based Electrophosphorescent Devices

X. GONG, M. R. ROBINSON, J. C. OSTROWSKI, D. MOSES, G. C. BAZAN and A. J. HEEGER, *Adv. Mater.*, 2002, 14, (8), 581–585

[Ir(DPF)₃] (DBF = 9,9-dihexyl-2-(pyridinyl-2')fluorene) and copolymers of poly(*N*-vinylcarbazole)/2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PVK/PBD) exhibit high efficiency electrophosphorescence. The highest external quantum efficiency of 10% photon/electron occurred with 0.3 wt.% [Ir(DPF)₃] in PVK/PBD (40 wt.%). OLEDs with luminous efficiencies $\leq 36 \text{ cd A}^{-1}$ at 45 V can be achieved.

Green Electrochemiluminescence from Ortho-Metalated Tris(2-phenylpyridine)iridium(III)

D. BRUCE and M. M. RICHTER, *Anal. Chem.*, 2002, 74, (6), 1340–1342

Ir(ppy)₃ (1) exhibits electrochemiluminescence (ECL) in CH₃CN, CH₃CN/H₂O and aqueous (0.1 M KH₂PO₄) solutions with tri-*n*-propylamine as an oxidative-reductive coreactant. ECL efficiencies (ϕ_{ECL}) of 0.00092 in aqueous, 0.0044 in mixed and 0.33 in CH₃CN solutions for (1) were obtained using Ru(bpy)₃²⁺ as a relative standard ($\phi_{\text{ECL}} = 1$). Photoluminescence efficiencies of 0.039, 0.050 and 0.069 were obtained in aqueous, mixed and CH₃CN solutions, respectively, compared to Ru(bpy)₃²⁺ ($\phi_{\text{em}} = 0.042$).

APPARATUS AND TECHNIQUE

Effect of Humidity on the Response Characteristics of Luminescent PtOEP Thin Film Optical Oxygen Sensors

K. EATON and P. DOUGLAS, *Sens. Actuators B, Chem.*, 2002, 82, (1), 94–104

The effect of humidity on the sensitivity of luminescent Pt octaethylporphyrin thin film O₂ sensors when the matrix is a hydrophilic polymer was examined. When ethyl cellulose (EC) is the matrix sensitivity is almost halved at 85% relative humidity (RH) as compared to 0% RH, whilst for cellulose acetate butyrate the sensitivity is reduced by 14% at 85% RH. For EC, the humidity dependence can be removed by a tributylphosphate plasticiser. For silicones, PVC and PS, humidity is not important.

Novel Electrode System for Electroflotation of Wastewater

X. CHEN, G. CHEN and P. L. YUE, *Environ. Sci. Technol.*, 2002, 36, (4), 778–783

The electrochemical stability of Ti/IrO_x-Sb₂O₅-SnO₂ anodes (1) containing only 2.5 mol% IrO_x was shown by accelerated life tests to be higher than that for the conventional Ti/IrO_x anode. CV studies showed that (1) could provide fast electron transfer. (1) were designed to be fork-like and interlocking at the same level as the cathode with a similar shape. This allows bubbles produced at both electrodes to be dispersed into the wastewater flow quickly, enhancing the effective contact between bubbles and particles – favourable for high flotation efficiency.

Voltammetric Microanalysis of DNA Adducts with Osmium Tetroxide, 2,2'-Bipyridine Using a Pyrolytic Graphite Electrode

M. FOJTA, L. HAVRAN, R. KIZEK and S. BILLOVÁ, *Talanta*, 2002, 56, (5), 867–874

DNA and synthetic polynucleotides modified with a complex of Os tetroxide with 2,2'-bipyridine (Os₄bipy) give specific voltammetric signals at pyrolytic graphite electrodes. Os₄bipy-modified DNA (DNA-Os₄bipy) can be determined in an excess of the free reagent. This is based on there being a sufficient potential separation between the peaks of DNA-Os₄bipy and free Os₄bipy, and using an adsorptive transfer stripping voltammetric procedure that involves extraction of free Os₄bipy from the electrode by CHCl₃.

HETEROGENEOUS CATALYSIS

Effects of Ce Addition and Pt Precursor on the Activity of Pt/Al₂O₃ Catalysts for Wet Oxidation of Phenol

S.-K. KIM and S.-K. IHM, *Ind. Eng. Chem. Res.*, 2002, 41, (8), 1967–1972

Pt was impregnated on γ -Al₂O₃ by using H₂PtCl₆ (1) and Pt(NH₃)₄Cl₂ (2). Pt/Al₂O₃ from (1) showed much higher activity for the wet oxidation of phenol than that from (2), because (1) gave a better metal dispersion. Ce addition lowered the catalytic activity of Pt/Al₂O₃ from (1), while it improved the activity of Pt/Al₂O₃ from (2).

Hydrosilylation of Alkynes Catalyzed by Platinum on Carbon

M. CHAUHAN, B. J. HAUCK, L. P. KELLER and P. BOUDJOUK, *J. Organomet. Chem.*, 2002, 645, (1–2), 1–13

Hydrosilylation of terminal and internal alkynes with chlorosilanes, alkylsilanes and alkoxy silanes was catalysed by Pt/C. The yields of the vinylsilanes were high and the selectivity of the product depended on the silane employed. Hydrosilylation of alkynes with chlorosilanes gave β -*trans* vinylsilanes, while alkyl- and alkoxy silanes gave 2–3 vinylsilane isomers.

Catalytic Hydrodechlorination of Chlorinated Olefins over a Pd/Al₂O₃ Catalyst: Kinetics and Inhibition Phenomena

S. ORDÓÑEZ, F. V. DÍEZ and H. SASTRE, *Ind. Eng. Chem. Res.*, 2002, 41, (3), 505–511

The gas phase hydrodechlorination of tetrachloroethene (TTCE), trichloroethene (TCE) and 1,1-dichloroethene (DCE) in toluene over commercial 0.15% Pd/Al₂O₃ was studied in a fixed bed reactor at 175–300°C for single compounds and at 250°C for mixtures. The order in reactivity was: DCE > TCE > TTCE. The influence of temperature on the kinetics can be modelled by a pseudo-first-order model and by considering an Arrhenius dependence for the kinetic constant. Inhibition phenomena were found by the studies involving mixtures.

The Treatment of Binary VOC Mixtures by Adsorption and Oxidation Using Activated Carbon and a Palladium Catalyst

E. KULLAVANIJAYA, N. W. CANT and D. L. TRIMM, *J. Chem. Technol. Biotechnol.*, 2002, 77, (4), 473–480

The adsorption of binary thiophene-containing mixtures (1) on activated C and their subsequent desorption and oxidation over Pd/CeO₂/Al₂O₃ were studied as a model for the treatment of dilute VOC streams by intermittent accumulation and combustion. Oxidation of (1) was controlled by thiophene oxidation which required > 300°C for complete removal. Both components of (1) can be removed by a system in which the VOCs are accumulated on C and then undergo temperature programmed desorption in air on Pd/CeO₂/Al₂O₃ at 350°C.

The Role of Bismuth as Promoter in Pd–Bi Catalysts for the Selective Oxidation of Glucose to Gluconate

M. WENKIN, P. RUIZ, B. DELMON and M. DEVILLERS, *J. Mol. Catal. A: Chem.*, 2002, 180, (1–2), 141–159

Pd–Bi/C catalysts of various Bi–Pd compositions (0.33 ≤ Bi:Pd ≤ 3.0, 10 wt.% Pd + Bi) were prepared from acetate-type precursors and analysed by XRD and XPS. In the selective oxidation of glucose to gluconate, the formation of Bi–glucose or Bi–gluconate complexes in the basic reaction medium is postulated. These Bi complexes may also be generated at the catalyst surface. The performance of the Pd/C catalyst is significantly improved by soluble Bi.

Preferential Catalytic Hydrogenation of Aromatic Compounds Versus Ketones with a Palladium Substituted Polyoxometalate as Pre-catalyst

V. KOGAN, Z. AIZENSHTAT and R. NEUMANN, *New J. Chem.*, 2002, 26, (3), 272–274

K₅PPdW₁₁O₃₉·12H₂O supported on γ -Al₂O₃ or C (1) was used as a catalyst precursor for hydrogenation. (1) achieved fast hydrogenation of arenes at 30 bar H₂ and 230°C. Arenes could be selectively reduced in the presence of distal ketone groups at 30 bar H₂ and 200°C. Also, aromatic compounds with vicinal (conjugated) ketone moieties underwent complete hydrogenation to saturated hydrocarbons.

Preparation of Rhodium Catalysts on Laminar and Zeolitic Structures by Anchoring of Organometallic Rhodium

C. BLANCO, R. RUIZ, C. PESQUERA and F. GONZÁLEZ, *Appl. Organomet. Chem.*, 2002, 16, (2), 84–93

Rh aluminosilicate catalysts were prepared by H₂ reduction of a cationic Rh complex anchored to the support. The precursor active phase was incorporated in acetone through ion exchange using [Rh(Me₂CO)_x(2,5-norbornadiene)]ClO₄. A higher Ru metal content was obtained in the supports with laminar structures, whereas a better dispersion was shown by catalysts supported on zeolitic structures.

New Preparation of Ru-Sn/Y Zeolite Catalyst for the Formation of Acetic Acid (Methyl Acetate) from Methanol Alone

T. OHNISHI, T. YAMAKAWA and S. SHINODA, *Appl. Catal. A: Gen.*, 2002, 231, (1–2), 27–33

Ru-Sn/Y zeolite catalysts (1) were prepared by: (a) the evacuation of $[\text{Ru}(\text{NH}_3)_6]^{3+}/\text{Y}$ to form Ru particles in the zeolite cavities; (b) the reaction of Cl_2 and Ru particles to form RuCl_n species in the cavities; and (c) introducing SnCl_2 as a vapour. The MeOH conversion at 473 K gave methyl acetate and H_2 after an induction period. Stationary activity was sustained for 200 h. The best yield of methyl acetate was $\leq 10.9\%$.

HOMOGENEOUS CATALYSIS

Pd-Catalysed Coupling Reactions in Supercritical Carbon Dioxide and under Solventless Conditions

N. SHEZAD, A. A. CLIFFORD and C. M. RAYNER, *Green Chem.*, 2002, 4, (1), 64–67

The homocoupling of iodoarenes to form biphenyl derivatives catalysed by $\text{Pd}(\text{OCOCF}_3)/\text{P}(2\text{-furyl})_3$ occurs best in sc-CO_2 and under solventless reaction conditions than in toluene. Diisopropylethylamine was used as the base. Reactions were carried out at 75°C in a high-pressure reaction vessel. A comparison of the results proposed that preferential solvation effects occurred in sc-CO_2 . Each of the methods investigated has advantages and disadvantages which need to be carefully considered before the method of choice is determined.

Palladium Catalysed Copolymerisation of Ethene with Alkylacrylates: Polar Comonomer Built into the Linear Polymer Chain

E. DRENT, R. VAN DIJK, R. VAN GINKEL, B. VAN OORT and R. I. PUGH, *Chem. Commun.*, 2002, (7), 744–745

Copolymerisation of ethene and alkylacrylates is catalysed by $\text{Pd}(\text{OAc})_2$ or $\text{Pd}(\text{dba})_2$ modified with di(2-methoxyphenyl)phosphinobenzene-2-sulfonic acid. NMR analysis of the copolymer shows that $\sim 10\%$ of the acrylate units have been incorporated into the linear polyethylene backbone. This is consistent with a mechanism that involves direct ethene insertion into the *in situ* formed Pd chelate catalyst.

The First Example of Palladium Catalysed Non-perfectly Alternating Copolymerisation of Ethene and Carbon Monoxide

E. DRENT, R. VAN DIJK, R. VAN GINKEL, B. VAN OORT and R. I. PUGH, *Chem. Commun.*, 2002, (9), 964–965

Non-alternating ethene-CO copolymerisation is catalysed by a new series of $[\text{P}-\text{O}]\text{Pd}$ catalysts (1) based on *o*-alkoxy derivatives of diphenylphosphinobenzene sulfonic acid (2). (1) were obtained by the *in situ* combination of (2) with $\text{Pd}(\text{OAc})_2$. The degree of non-alternation (observed by $^{13}\text{C}\{^1\text{H}\}$ NMR analysis) can be tuned by reaction temperature, relative ethene and CO concentrations, and ancillary ligand.

Palladium-Catalyzed Asymmetric Synthesis of Cyclohexene Derivatives Having the Substituents at the 2-Position and the Application to the Syntheses of the Natural Products

M. MORI, *J. Synth. Org. Chem., Jpn.*, 2002, 60, (1), 15–25

The asymmetric synthesis of 2-arylcyclohexene derivatives was achieved via a π -allyl-Pd complex generated from 2-arylcyclohexenol derivatives, $\text{Pd}(0)$ and (*S*)-BINAPO. (–)-Mesembrine, (–)-mesembrane, (+)-crinamine, (–)-haemanthidine and (+)-pretazettine were synthesised. Treatment of the cyclohexanol derivative (having a silyloxymethyl group at the 2-position) with *N*-tosyl-*o*-bromoaniline in the presence of $\text{Pd}_2\text{dba}_3\cdot\text{CHCl}_3$ and (*S*)-BINAPO gave the cyclohexenylamine derivative with 84% ee in 76% yield. The silyloxymethyl group was converted into the cyanomethyl group and the resulting compound was treated with $\text{Pd}(\text{OAc})_2$ and PMe_2Ph to give the indole derivative.

The Heck Reaction with Unprotected Allylic Amidines and Guanidines

E. C. LAWSON, W. A. KINNEY, D. K. LUCI, S. C. YABUT, D. WISNOSKI and B. E. MARYANOFF, *Tetrahedron Lett.*, 2002, 43, (11), 1951–1953

Using Heck methodology, unprotected guanidine-substituted olefins, such as allylaminoimidazoline, were coupled to aryl iodides. A Pd catalyst was formed *in situ* from $\text{Pd}(\text{OAc})_2$ and $\text{P}(o\text{-tolyl})_3$. A highly functionalised iodoquinazolinone was then employed as a substrate in a series of Heck coupling reactions, to provide an efficient synthesis of a new class of vitronectin receptor antagonists.

A New Catalytic Hetero-Heck Type Reaction

J. HELAJA and R. GÖTTLICH, *Chem. Commun.*, 2002, (7), 720–721

Unsaturated *N*-chloroamines are cyclised to piperidines using $\text{Pd}(\text{PPh}_3)_4$ (1) as the catalyst at room temperature. Reducing the amount of (1) from 10 to 5 or 1% led to an increased yield of the reaction product. $\text{Rh}(\text{I})$, $\text{Ir}(\text{I})$ and $\text{Ni}(0)$ complexes can also be used as efficient catalysts. The metal amide intermediates cannot be isolated as they undergo β -hydride elimination.

Rhodium-Catalyzed Hydroarylation and -Alkenylation of Alkynes with Silanediols.

A Crucial Role of the Hydroxy Group for the Catalytic Reaction

T. FUJII, T. KOIKE, A. MORI and K. OSAKADA, *Synlett*, 2002, (2), 295–297

Aryl- and alkenylsilanediols, which have 2 OH groups on the Si atom, undergo the Rh-catalysed addition of an organic group on Si to internal alkynes. The reaction of internal alkynes with aryl- or alkenylsilanediols in the presence of 3 mol% of $[\text{Rh}(\text{OH})(\text{cod})]_2$ gave hydroarylated or hydroalkenylated products in good yields.

Polymerization of Phenylacetylene by Iridium

Catalysts

K. KANKI, Y. MISUMI and T. MASUDA, *J. Polym. Sci. A: Polym. Chem.*, 2002, 40, (8), 1075–1080

$[(\text{cod})\text{IrCl}_2]/n\text{-BuLi}$ and $[(\text{cod})\text{IrCl}_2]/\text{Ph}_2\text{C}=\text{C}(\text{Ph})\text{Li}$ induce the polymerisation of phenylacetylene to give polymers with a number-average molecular weight (M_n) of ~ several thousand in rather low yields. In contrast, the system $[(\text{cod})\text{IrCl}_2]/\text{norbornadiene}/\text{Ph}_3\text{P}/\text{Ph}_2\text{C}=\text{C}(\text{Ph})\text{Li}$ (molar ratio of 1:1:1.1:2) gave a polymer with $M_n > 100,000$ in high yield (~ 80%) in toluene at 0°C. The side reaction was depressed.

Carbon–Carbon Bond Formation by Reactions of Allylic Alcohol with Enoxysilane in the Presence of Ir-Complex

I. MATSUDA, S. WAKAMATSU, K. KOMORI, T. MAKINO and K. ITOH, *Tetrahedron Lett.*, 2002, 43, (6), 1043–1046

Substitution of allylic alcohols to form a C–C bond is achieved by reaction of the allylic alcohol itself with an enoxysilane, catalysed by $[\text{Ir}(\text{cod})(\text{PPh}_3)_2]\text{X}$ (1). (1) is activated in advance by H_2 to form a C–O bond or a C–C bond at the allylic position. The anion X of (1) enhances the rate and product yields of the reactions in the order of: $\text{PF}_6^- < \text{ClO}_4^- < \text{TfO}^-$. The reactions were carried out in CH_2Cl_2 .

Preparation of Cyclic Ethers for Polyether Synthesis by Catalytic Ring-Closing Enyne Metathesis of Alkynyl Ethers

J. S. CLARK, F. ELUSTONDO, G. P. TREVITT, D. BOYALL, J. ROBERTSON, A. J. BLAKE, C. WILSON and B. STAMMEN, *Tetrahedron*, 2002, 58, (10), 1973–1982

Alkenyl-substituted six and seven-membered cyclic enol ethers, which are potential building blocks for the synthesis of marine polyether natural products, were prepared in high yield (70–97%) from alkynyl ethers by Ru-catalysed ring-closing enyne metathesis. The catalysts are carbene-bearing Ru complexes and are tolerant of a wide range of alkyne substituents.

Amine Additives for Fast Living Radical Polymerization of Methyl Methacrylate with $\text{RuCl}_2(\text{PPh}_3)_3$

S. HAMASAKI, M. KAMIGAITO and M. SAWAMOTO, *Macromolecules*, 2002, 35, (8), 2934–2940

Appropriate secondary and tertiary amines are effective at enhancing the rate and controlling the living radical polymerisation of methyl methacrylate with $\text{RuCl}_2(\text{PPh}_3)_3$. This was caused by the *in situ* formation of a highly active amine-coordinated mononuclear Ru complex. With *n*-Bu₃N and *n*-Bu₂NH, the polymerisation of R–Cl/ $\text{RuCl}_2(\text{PPh}_3)_3$ in toluene at 80°C reached 90% conversion in 50 h and 94% in 20 h, respectively, but only 46% in 120 h without additives. The polymers obtained with the amine additives had controlled molecular weights which increased in direct proportion to the monomer conversion, and also had narrow MWDs ($M_w/M_n = 1.1\text{--}1.2$).

FUEL CELLS

In-Situ XANES of Carbon-Supported Pt–Ru Anode Electrocatalyst for Reformate-Air Polymer Electrolyte Fuel Cells

R. VISWANATHAN, G. HOU, R. LIU, S. R. BARE, F. MODICA, G. MICKELSON, C. U. SEGRE, N. LEYAROVSKA and E. S. SMOTKIN, *J. Phys. Chem. B*, 2002, 106, (13), 3458–3465

In situ XANES experiments were carried out on a working reformate-air fuel cell to study the structure of the Pt–Ru/C anode electrocatalyst. The fuel cell was operated in a normal mode. A fresh MEA and a conditioned MEA were employed at different operating conditions of the fuel cell and different feed (pure H_2 or H_2/CO (100 ppm)) at the anode. The *in situ* Pt L_{III}-edge and Ru K-edge XANES of the fuel cell MEAs exhibited metallic characteristics.

ELECTRICAL AND ELECTRONIC ENGINEERING

Etch Characteristics of Pt by Using BCl_3/Cl_2 -Gas Mixtures

K.-H. KWON, S.-Y. KANG, S.-I. KIM and N.-K. HONG, *J. Mater. Sci.: Mater. Electron.*, 2002, 13, (4), 187–191

The inductively coupled plasma etching of Pt with BCl_3/Cl_2 -gas was studied. Although the relative radical density and ion current density at the Cl_2 ratio of 100% are lower than those at the Cl_2 ratio of 75%, the etch rate of Pt can be higher in pure Cl_2 -gas plasma. The B plays the role of an etch-resistive element in the Cl_2 -gas plasma. The B dissociated from BCl_3 is adsorbed on the etched Pt surface, combines with Cl species, forms BCl_x ($x \leq 3$) and this is finally easily vapourised due to its high vapour pressure.

Ti_xZr_{1-x} Underlayers for CoCrPtB Perpendicular Magnetic Recording Media

Y.-N. HSU, K. W. WIEMAN, B. LU, T. J. KLEMMER and J. K. HOWARD, *IEEE Trans. Magn.*, 2002, 38, (2), 1436–1440

The addition of 40 and 60 at.% of Zr to Ti underlayers improved the Ti_xZr_{1-x} (0002) texture. This further enhanced the CoCrPtB (0002) texture when the CoCrPtB magnetic layers were deposited onto the Ti₄Zr₆ and Ti₆Zr₄ underlayers. The coercivity and squareness of the CoCrPtB layers deposited on the pure Ti and Zr underlayers were higher than those on the TiZr alloy underlayers.

Effects of Substrate-Bias on the Structure of Sputter-Deposited Co–Pt Film

T. SHINMITSU, J. SHI and M. HASHIMOTO, *Surf. Coat. Technol.*, 2002, 151–152, 55–58

Co–Pt films (1) were deposited by DC-sputtering onto (001)-oriented Si wafer substrates. (1) deposited at room temperature are composed of a disordered Co–Pt phase of f.c.c. structure. Substrate bias during sputter deposition alters the composition of (1) through the preferential resputtering of Co. The crystalline quality of (1) is improved significantly by increasing the substrate bias up to –150 V.