ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Control of the Magnetic Anisotropy of a Co/Pt Nanomultilayer with Embedded Particles

I.-J. JEON, D.-W. KANG, D.-E. KIM, D.-H. KIM, S.-B. CHOE and S.-C. SHIN, *Adv. Mater.*, 2002, 14, (16), 1116–1120

Co/Pt nanomultilayers with embedded particles were shown to have different magnetic characteristics compared with particle-free samples (made by a magnetron sputtering system) of almost the same structure. This is particularly with respect to having:
(a) smaller coercivity fields, (b) biaxial magnetic anisotropies and (c) the existence of a critical field at which the easy direction changes from the parrallel direction to a perpendicular direction and vice versa.

Martensitic Transformation in Pd-Rich Fe-Pd-Pt Alloy

T. WADA, T. TAGAWA and M. TAYA, Sor. Mater., 2003, 48, (2), 207-211

The replacement of Pd with Pt in an Fe-30 at.% Pd alloy decreased the f.c.c./f.c.t. martensite transformation temperature. Strengthening due to solution hardening with Pt was observed. The shape memory effects of Fe-(xPdyPt)_{x+y=30} at.% alloys with ≤ 4 at.% Pt were investigated below the austenite finishing temperatures.

Improvement of Shape Memory Characteristics in Fe-Pd Melt-Spun Shape Memory Ribbons

D. VOKOUN and C. T. HU, J. Alloys Compd., 2002, 346, (1-2), 147-153

An Fe-Pd alloy with ~ 30 at.% Pd and with or without very small amounts of the b.c.t. phase exhibits shape memory properties with transformation temperatures \sim room temperature. The use of the free jet melt-spinning method in manufacturing the Fe-Pd ribbons was effective in suppressing the presence of b.c.t. martensite. This was due to rapid solidification.

Two-Directional N₂ Desorption in Thermal Dissociation of N₂O on Rh(110), Ir(110), and Pd(110) at Low Temperatures

H. HORINO, I. RZEŹNICKA, A. KOKALJ, I. KOBAL, Y. OHNO, A. HIRATSUKA and T. MATSUSHIMA, J. Vac. Sci. Technol. A, 2002, 20, (5), 1592–1596

Two-directional N_2 desorption was found in N_2O dissociation on Rh(110), Ir(110) and Pd(110) at < 160 K by angle-resolved thermal desorption. $N_2O(a)$ is mostly dissociated during heating, emitting $N_2(g)$ and leaving O(a). N_2 showed four desorption peaks at 110–200 K. One of them commonly shows a cosine distribution due to desorption from $N_2(a)$. N_2 desorbing in the other peaks sharply collimates off the surface normal in the plane along the [001] direction.

CHEMICAL COMPOUNDS

Metallabenzenes and Valence Isomers.

Synthesis and Characterization of a Platinabenzene V. JACOB, T. J. R. WEAKLEY and M. M. HALEY, Angew. Chem. Int. Ed., 2002, 41, (18), 3470–3473

The synthesis of the first example of a platinabenzene (1) has been achieved. [Pt(cod)Cl₂] was treated with a nucleophile 3-vinylcyclopropene to give (1), which was fully characterised by NMR spectroscopy and X-ray crystallography. (1) contains two different rearrangement products of the vinylcyclopropene precursor.

Polymer Complexes of Rhodium(II) Trifluoroacetamidate with Pyrazine, 4,4'-Bipyridine, and 1,4-Diazabicyclo[2.2.2]octane

M. HANDA, Y. MURAKI, M. MIKURIYA, H. AZUMA and K. KASUGA, *Bull. Chem. Soc. Jpn.*, 2002, 75, (8), 1755–1756 Polymer complexes, [{Rh₂(HNOCCF₃)₄(L)}_n] (L = pyrazine, 4,4'-bipyridine (4,4'-bpy), 1,4-diazabicy-clo[2.2.2]octane), of Rh(II) trifluoroacetamide dimers bridged by bidentate ligands were prepared and characterised. For [{Rh₂(HNOCCF₃)₄(4,4'-bpy)}_n], the crystallographic inversion centre is located at the centre of the dimer core. The chain structure is built up by the alternating arrangement of the Rh₂ dimer and 4,4'-bpy.

Kinetic Analysis and Solvent Effects in the Carbonylation of $RuCl_3-3H_2O$

R. TANNENBAUM, J. Phys. Chem. A, 2002, 106, (41), 9502–9505. The carbonylation of RuCl₃·3H₂O in refluxing alcohol represents the entry point to Ru organometallic chemistry. The overall carbonylation reaction is composed of three consecutive reactions, each step resulting in a Ru carbonyl complex with different Ru:CO ratios. A kinetic analysis of the overall reaction revealed the parameters involved in the rates of formation of each compound, and as a result, provides a method to control the product composition.

Triple C-H Activation of 1,5-Bis(di-*tert*-butylphosphino)-2-(*S*)-dimethylaminopentane on Ruthenium Gives a Chiral Carbene Complex

V. F. KUZNETSOV, A. J. LOUGH and D. G. GUSEV, *Chem. Commun.*, 2002, (20), 2432–2433

A novel trans-chelating diphosphine, 1,5-bis(di-tert-butylphosphino)-2-(S)-dimethylaminopentane (1), 'pincer' ligand, was prepared in five steps. (1) underwent triple C-H activation in reaction with [RuCl₂(p-cymene)]₂ to give a chiral square-pyramidal 16-electron carbene complex of Ru (2). (2) was isolated in 79% yield as air sensitive thin red needles soluble in common organic solvents.

PHOTOCONVERSION

Light-Emitting Cyclopalladated Complexes of 6-Phenyl-2,2'-bipyridines with Hydrogen-Bonding Functionality

F. NEVE, A. CRISPINI, C. DI PIETRO and S. CAMPAGNA, Organometallics, 2002, 21, (17), 3511-3518

Cyclometallated Pd(II) complexes [Pd(Ln)Cl] (n = 1–3) were prepared using HL1 = 4-carboxy- (1), HL2 = 4-carboxyphenyl- (2) and HL3 = 4-hydroxyphenyl-6-phenyl-2,2'-bipyridine (3). All the complexes (1–3) exhibited intense luminescence at 77 K, with lifetimes of 10–200 µs. (1) gave room temperature solid-state luminescence (emission at 650 nm and lifetime of 1 µs), due to oligomeric species.

Divalent Osmium Complexes: Synthesis, Characterization, Strong Red Phosphorescence, and Electrophosphorescence

B. CARLSON, G. D. PHELAN, W. KAMINSKY, L. DALTON, X. JIANG, S. LIU and A. K.-Y. JEN, *J. Am. Chem. Soc.*, 2002, 124, (47), 14162–14172

Red-emitting Os(II)(N-N)₂L-L (1) (N-N = bipy or phen derivative; L-L = phosphine or arsine) were synthesised. (1) feature strong MLCT absorption bands in the visible region and strong red phosphorescent emission at 611-651 nm, with quantum yields ≤ 45%. Red OLEDs were fabricated by doping (1) into a blend of poly(N-vinylcarbazole) and 2-tert-butylphenyl-5-biphenyl-1,3,4-oxadiazole.

High-Brightness and Low-Voltage Light-Emitting Devices Based on Trischelated Ruthenium(II) and Tris(2,2'-bipyridine)osmium(II) Emitter Layers and Low Melting Point Alloy Cathode Contacts

F. G. GAO and A. J. BARD, Chem. Mater., 2002, 14, (8), 3465-3470

LEDs were fabricated based on an amorphous film of Ru(bpy)₃(ClO₄)₂ (~ 100 nm thick) on ITO with printed low melting point alloys, such as Ga:In, Ga:Sn and Bi:In:Pb:Sn, as cathodic contacts. A device of structure: ITO (\leq 10 Ω /square)/Ru(bpy)₃(ClO₄)₂/Ga:Sn gave red emission (3500 cd m⁻² at 4.0 V) at 660 nm. C₁₂–Ru(bpy)₃(ClO₄)₂, Ru(phenanthroline)₃(ClO₄)₂ and Os(bpy)₃(PF₆)₂ were also used for LEDS.

Efficient Panchromatic Sensitization of Nanocrystalline TiO₂ Films by β-Diketonato Ruthenium Polypyridyl Complexes

A. ISLAM, H. SUGIHARA, M. YANAGIDA, K. HARA, G. FUJIHASHI, Y. TACHIBANA, R. KATOH, S. MURATA and H. ARAKAWA, *New J. Chem.*, 2002, **26**, (8), 966–968

Ru(4,4',4"-tricarboxy-2,2':6',2"-terpyridine)(1,1,1-trifluoropentane-2,4-dionato)(NCS) and Ru(4,4',4"-tricarboxy-2,2':6',2"-terpyridine)(1,1,1-trifluoroeicosane-2,4-dionato)(NCS) when anchored to nanocrystalline TiO₂ films achieve very efficient panchromatic sensitisation. This is over the whole visible range extending into the near IR region, yielding 70% incident photon to current conversion efficiencies.

ELECTRODEPOSITION AND SURFACE COATINGS

Electrodeposition of Rhodium Metal on Titanium Substrates

A. M. BARAKA, H. H. SHAARAWY and H. A. HAMED, Anti-Corrosion Methods Mater., 2002, 49, (4), 277-282

Ti substrates were pre-anodised in oxalic acid solution (100 g Γ^1) at high current density of 60–95 mA cm⁻² and at ambient temperature. A thin, porous and conductive Ti oxide film was obtained which could then be electroplated with Rh. Rh metal was electrodeposited over the anodised Ti substrates from a bath consisting of Rh₂(SO₄)₃ (5.2 g Γ^1) and H₂SO₄ (100 g Γ^1). Rh electrodeposits with high adhesion and brightness can be achieved.

Plasma Based Ion Implantation Technology for High-Temperature Oxidation-Resistant Surface Coatings

S. ISOGAWA, H. TOJO, A. CHAYAHARA and Y. HORINO, *Surf. Coat. Technol.*, 2002, 158–159, 186–192

Ir-Re alloy surface coatings (1) were produced by plasma-based ion implantation (PBII) technology, using a coaxial type arc-vacuum metal-plasma source. (1) were used to prevent surface oxidation of WC alloy engineering tools at high temperature. The sticking strength of the PBII-films is similar to that of films prepared by a conventional sputtering method (SP-films). Microscopic exfoliation was observed at the SP-films, but no exfoliation was observed at the PBII-films.

APPARATUS AND TECHNIQUE

Fabrication of Sharp Tetrahedral Probes with Platinum Coating

M. KITAZAWA and A. TODA, Jpn. J. Appl. Phys., Part 1, 2002, 41, (7B), 4928–4931

Metal-deposited cantilever probes (1) with a 13 nm tip radius for conducting scanning probe microscopy are obtained by sputter coating a Si cantilever with Pt on a single side. (1) are free from cantilever curling and have 350 Ω probe resistance on average. Al was deposited as a reflex coating on the back of (1).

Analytical Performance of a Glucose Biosensor Prepared by Immobilization of Glucose Oxidase and Different Metals into a Carbon Paste Electrode S.A. MISCORIA G. D. BARRERA and G. A. RIVAS. Flettmandwis.

S. A. MISCORIA, G. D. BARRERA and G. A. RIVAS, *Electroanalysis*, 2002, 14, (14), 981–987

Enzymatic metallised C paste electrodes (CPEs) prepared by incorporation of metal mixtures into the paste offer a substantial decrease in the overvoltage for H_2O_2 oxidation and reduction. Combining Ir into CPE containing glucose oxidase with Pd, Cu or Ru gave enhancements in sensitivity and selectivity. A linear relationship between current and glucose concentration was obtained at $\leq 1.5 \times 10^2$ M glucose for a Pd(2.65%)-Ir(8.00%)-glucose oxidase(7.00%)-CPE.

HETEROGENEOUS CATALYSIS

Low-Temperature Catalytic Decomposition of N₂O on Platinum and Bismuth-Modified Platinum: Identification of Active Sites

R. BURCH, G. A. ATTARD, S. T. DANIELLS, D. J. JENKINS, J. P. BREEN and P. HU, *Chem. Commun.*, 2002, (22), 2738–2739

Surface modification of 5% Pt/C with Bi was carried out by irreversible adsorption of aqueous Bi ions from a Bi nitrate solution. The Bi/5% Pt/C catalysts were used to identify the active centres on Pt for N₂O decomposition. Terrace sites were not active for this reaction, whereas edge or defect sites appeared to be the active sites. Thus, in contrast to NO dissociation on Rh, where large metal particles are favoured, for Pt, the highest activity for N₂O dissociation occurs on very small metal particles.

Catalyst–Support Interaction in Fluorinated Carbon-Supported Pt Catalysts for Reaction of NO with NH₃

W. AN, K. T. CHUANG and A. R. SANGER, *J. Catal.*, 2002, 211, (2), 308–315

Pt/fluorinated C (0, 10, 28 and 65% F) catalysts (1) were characterised and their activities were compared for the reaction of NO with NH₃. Optimum activity and selectivity were found for (1) when the support has 28% F. Above this F content, catalytic activity is inhibited due to blocking of the Pt sites. The increase in selectivity with (1) is due to the electronic interaction between the fluorinated C and Pt which gives rise to enhanced dissociative chemisorption of NO on active Pt sites.

Dehydrogenation of Neohexane to Neohexene on Platinum Polymetallic Catalysts

S. B. KOGAN and M. HERSKOWITZ, Ind. Eng. Chem. Res., 2002, 41, (24), 5949–5951

Selective dehydrogenation of neohexane to neohexene was carried out on Pt polymetallic catalysts and Cr supported catalysts (1) in steam at 520–550°C. Pt-Sn-K/Al₂O₃ and Pt-Sn-K-Fe/Al₂O₃ (2) gave similar initial performances of high selectivity of 83 mol%, significantly higher than those of (1). (2) with Fe has much better long-term stability, in 26 cycles, and was regenerated by steam treatment at 550°C.

Membrane Reactor Microstructured by Filamentous Catalyst

L. KIWI-MINSKER, O. WOLFRATH and A. RENKEN, *Chem. Eng. Sci.*, 2002, 57, (22–23), 4947–4953

A microstructured membrane reactor (1) with micro-channels formed between closely packed catalytic filaments, 7 μ m in diameter, of Pt/Sn on Al₂O₃ has been designed. (1) with a Pd/Ag membrane was used in non-oxidative propane dehydrogenation. The catalytic filaments were active/selective and withstood periodic regeneration. At propane conversions exceeding equilibrium, selectivities towards propene \leq 97% were obtainable.

Heterogeneous Pd-Catalyzed Biphenyl Synthesis under Moderate Conditions in a Solid–Liquid Two-Phase System

S. MUKHOPADHYAY, S. RATNER, A. SPERNAT, N. QAFISHEH and Y. SASSON, Org. Process Res. Dev., 2002, 6, (3), 297–300

The coupling of substituted halobenzenes to give biphenyls was achieved at 65°C using a reducing agent, such as a formate salt, and NaOH, in the presence of tetrabutylammonium bromide phase-transfer catalyst and 5% Pd/C catalyst. The occurrence of a competing hydrodehalogenation reaction was minimised by altering the process variables. The highest selectivity to biphenyl was 71%. The solid Pd/C catalyst was recycled without losing its catalytic activity by filtration and washing with MeOH.

Novel Biomass Gasification Method with High Efficiency: Catalytic Gasification at Low Temperature M. ASADULLAH, T. MIYAZAWA, S. ITO, K. KUNIMORI,

M. YAMADA and K. TOMISHIGE, *Green Chem.*, 2002, 4, (4), 385–389

Rh/CeO₂/SiO₂ (1) was shown to be an efficient catalyst for the gasification of biomass at 823–923 K in a fluidised bed continuous feeding reactor. This temperature range is much lower than conventional gasification methods (973–1073 K for catalytic and 1073–1223 K for non-catalytic). With (1), ~ 98% C conversion can be achieved. The tar was completely gasified and only a very small amount of char formed.

HOMOGENEOUS CATALYSIS

First Application of Secondary Phosphines as Supporting Ligands for the Palladium-Catalyzed Heck Reaction: Efficient Activation of Aryl Chlorides A. SCHNYDER, T. AEMMER, A. F. INDOLESE, U. PITTELKOW and

A. SCHNYDER, T. AEMMER, A. F. INDOLESE, U. PITTELKOW and M. STUDER, Adv. Synth. Catal., 2002, 344, (5), 495–498

Secondary dialkylphosphines (1) were employed as supporting ligands for the Pd-catalysed Heck reaching the process of the Pd-catalysed Heck reaching the process of the Pd-catalysed Heck reaching the pd-catalysed the pd-catalysed

supporting ligands for the Pd-catalysed Heck reactions of electron-rich and electron-poor aryl chlorides with olefins. PdCl₂ solution in concentrated HCl was used as the source of Pd. The yields with HP(t-butyl)₂ and HP(adamantyl)₂ were comparable or better than those with P(t-butyl)₃ and P(cyclohexyl)₃. (1) are readily available at low cost on a technical scale.

Synthesis of Monocarbenepalladium(0) Complexes and Their Catalytic Behavior in CrossCoupling Reactions of Aryldiazonium Salts

K. SELVAKUMAR, A. ZAPF, A. SPANNENBERG and M. BELLER, Chem. Eur. J., 2002, 8, (17), 3901–3906

The first monocarbenepalladium(0) complexes (1) having benzoquinone and naphthoquinone as additional ligands were prepared. (1) are air- and moisture-stable. NMR spectroscopy and X-ray analysis of (1) show a bidentate bonding mode of the quinone. When (1) were used as catalysts in Heck and Suzuki coupling reactions with aryldiazonium salts, yields > 90% were achieved.

Carbonylation Reactions of Iodoarenes with PAMAM Dendrimer-Palladium Catalysts Immobilized on Silica

S. ANTEBI, P. ARYA, L. E. MANZER and H. ALPER, *J. Org. Chem.*, 2002, **67**, (19), 6623-6631

Pd complexes, such as Pd(RCN)₂Cl₂ (R = Me, Ph) or Pd(tetramethylethylenediamine)Me₂, immobilised onto generation 0–3 PAMAM dendrimers supported on SiO₂ were used as catalysts for the carbonylation of iodobenzene in MeOH to form methyl benzoate. High yields were obtained and the catalyst was recycled 4–5 times without significant loss of activity.

Addition Polymerization of Norbornene-Type Monomers. High Activity Cationic Allyl Palladium Catalysts

J. LIPIAN, R. A. MIMNA, J. C. FONDRAN, D. YANDULOV, R. A. SHICK, B. L. GOODALL, L. F. RHODES and J. C. HUFFMAN, *Macromolecules*, 2002, 35, (24), 8969–8977

High activity cationic (η³-allyl)Pd catalysts (1) for the vinyl addition polymerisation of norbornene-type monomers have been developed. [(η³-allyl)Pd(tricy-clohexylphosphine)(ether)][B(3,5-(CF₃)₂(C₀H₃)₄] catalyst copolymerises 5-butylnorbornene and 5-triethoxysi-lylnorbornene (95:5 molar ratio) and is capable of producing more than a metric ton of copolymer per mole Pd per hour. (1) can be generated *in situ* by abstraction of leaving groups such as Cl⁻, CH₃CO₂⁻ and NO₃⁻ from Pd using a salt of a weakly coordinating anion.

Dendritic Nanoreactors Encapsulating Pd Particles for Substrate-Specific Hydrogenation of Olefins

M. OOE, M. MURATA, T. MIZUGAKI, K. EBITANI and K. KANEDA, $\it Nano Lett., 2002, 2, (9), 999-1002$

Dendrimer-encapsulated Pd(0) nanoparticles (2–3 nm diameter) inside poly(propylene imine) dendrimers functionalised with triethoxybenzamide were obtained by extraction of Pd²⁺ and subsequent chemical reduction with KBH₄. The resulting Pd-dendrimer nanocomposites were used as catalysts for substrate-specific hydrogenation of polar olefins.

Synthesis of Pyrimido[4,5-b]indoles and Benzo[4,5]furo[2,3-d]pyrimidines via Palladium-Catalysed Intramolecular Arylation

Y.-M. ZHANG, T. RAZLER and P. F. JACKSON, Tetrahedron Lett., 2002, 43, (46), 8235–8239

A Pd-catalysed intramolecular arylation of various pyrimidine substrates gave pyrimido[4,5-b]indoles and benzo[4,5]furo[2,3-d]pyrimidines. Thus, 4-aryloxy- or 4-anilino-5-iodopyrimidines were treated with Pd(OAc)₂(PPh₃)₂ and a base, such as NaOAc, Et₃N, Cs₂CO₃ and NaOBu', in DMF to give the regioselective cyclised heterocycles. A study of the influence of different solvents suggested that DMF (85°C) or DMA (100°C) were the best. No reaction was observed at \leq 70°C.

Ir and Rh Complex-Catalyzed Intramolecular Alkyne–Alkyne Couplings with Carbon Monoxide and Isocvanides

T. SHIBATA, K. YAMASHITA, E. KATAYAMA and K. TAKAGI, *Tetrabedron*, 2002, **58**, (43), 8661–8667

Catalytic intramolecular alkyne—alkyne couplings with CO and isocyanide have been developed. Carbonylative coupling was efficiently catalysed by Vaska's complex (IrCl(CO)(PPh₃)₂). Various diynes were transformed into bicyclic cyclopentadienones in good to high yields. The first catalytic synthesis of iminocyclopentadienes was achieved using [RhCl(cod)]₂ in alkyne—alkyne coupling with isocyanides. Portions of isocyanides were added at appropriate time intervals in Bu₂O.

Water-Gas Shift Reaction Catalyzed by Mononuclear Ruthenium Complexes Containing Bipyridine and Phenanthroline Derivatives

P. AGUIRRE, S. A. MOYA, R. SARIEGO, H. LE BOZEC and A. J. PARDEY, *Appl. Organomet. Chem.*, 2002, 16, (10), 597–600

[RuL(CO)₂Cl₂], [RuL₂Cl₂], [RuL₂(CO)(H₂O)](PF₆)₂, [RuL₂Cl]₂(PF₆)₂, [RuL₂(CO)Cl](PF₆) and [RuL₂(CO₃)]·3H₂O (L = bipy or phen derivative) with KOH, triethylamine or trimethylamine in aqueous 2-ethoxyethanol catalyse the WGSR. Mild conditions were used: P_{CO} = 0.9 atm at 100°C. Any ligand that increased the electronic density on the Ru, such as 6-methyl- and 6,6'-dimethyl-4,4'-di-*tert*-butyl-2,2'-bi-pyridine, produced a higher catalytic activity.

FUEL CELLS

Microwave-Assisted Synthesis of Carbon Supported Pt Nanoparticles for Fuel Cell Applications

W. X. CHEN, J. Y. LEE and Z. LIU, *Chem. Commun.*, 2002, (21), 2588–2589

Spherical and uniform Pt nanoparticles (1) (3.5–4 nm diameter) were prepared by microwave irradiation. Pt/C nanocomposites containing 10, 15 and 20 wt.% of Pt were also successfully prepared. (1) exhibited very high electrocatalytic activity in the room temperature oxidation of MeOH and are therefore useful in DMFC applications.

Electro-Oxidation of Ethanol on Pt, Rh, and PtRh Electrodes. A Study Using DEMS and in-Situ FTIR Techniques

J. P. 1. DE SOUZA, S. L. QUEIROZ, K. BERGAMASKI, E. R. GONZALEZ and F. C. NART, *J. Phys. Chem. B*, 2002, 106, (38), 9825–9830

Three products, CO_2 , acetaldehyde and acetic acid, were detected from the electrooxidation of EtOH by the title electrodes. Rh was the far less active electrocatalyst for EtOH electrochemical oxidation. Pure Pt and $Pt_{90}Rh_{10}$ gave similar normalised current densities, but $Pt_{90}Rh_{10}$ gave a better CO_2 yield than pure Pt. $Pt_{73}Rh_{27}$ electrodes gave the best CO_2 yield. The ratio CO_2 : CH_3CHO increases when Rh is added to the electrode.