

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

High-Temperature Creep of Pure Platinum

T. HAMADA, S. HITOMI, Y. IKEMATSU and S. NASU, *Mater. Trans. JIM*, 1996, 37, (3), 353–358

The creep behaviour of high purity Pt (99.999 mass%) was studied at 1373–1773 K. Pt showed the power-law creep with the stress exponent of the steady state rate being ~ 6 . Recrystallisation to bamboo-type grains from the initial polycrystalline micro-grains was observed. The creep rupture mechanism changed on recrystallisation from grain boundary fracture due to coalescence of the voids to rupture by necking or shearing-off. The activation energy for the steady state creep is $(3.1 \pm 0.3) \times 10^5$ J/mol.

Visualization and Analysis of Forced Diffusion of Hydrogen in Palladium by Electrotransport

M. TAMAKI, S. HARA, I. KONDOH, K. YONEDA, A. TSURUNO and H. KOBAYASHI, *Nucl. Instr. Methods Phys. Res. A*, 1996, 377, (1), 166–169

Hydrogen was electrotransported in Pd hydride by an applied electric field to densify H at the cathodic side. The effectiveness of the electrotransportation was studied by neutron radiography. The H:Pd concentration was enhanced to 0.75 ± 0.05 at 395 K, after 100 days using 0.31 MPa H_2 , which is equivalent to a H_2 equilibrium pressure of 100 MPa. The effective number of the electric charge of H in the Pd hydride (β) phase was 0.38 ± 0.08 .

Properties and Structures of Cu-16.67Pd and Cu-37.5Pd Alloys

J. MU, *Precious Met. (China)*, 1996, 17, (2), 12–17

Properties and structures of Cu-16.67Pd and Cu-37.5Pd alloys were studied by determining resistance, hardness, thermal analysis, TEM and XRD. The properties of the CuPd alloy were unusual. A Cu₃Pd ordered compound with a tetragonal structure was formed after prolonged heat treatment and Cu-37.5Pd was transformed into the b.c.c. phase.

Development of Ir-Base Refractory Superalloys

Y. YAMABE, Y. KOIZUMI, H. MURAKAMI, Y. RO, T. MARUKO and H. HARADA, *Scr. Metall. Mater.*, 1996, 35, (2), 211–215

A new class of Ir-base, refractory superalloys is described, which are alloys with γ -f.c.c. and γ' -L1₂ coherent structures similar to Ni-base superalloys, but with higher melting points. Ir-15 at.%Nb and Ir-15 at.%Ti refractory superalloys have γ/γ' coherent two-phase structures, high compressive strengths and enhanced oxidation resistance. Their 0.2% flow stresses at 1800°C were 210–220 MPa, equivalent to those of the strongest W-base refractory alloys.

CHEMICAL COMPOUNDS

Patterns of Multiple Additions to Fullerene C₇₀: Isolation and Structural Characterization of [C₇₀{Pt(PPh₃)₂]₄

A. L. BALCH, L. HAO and M. M. OLMSTEAD, *Angew. Chem., Int. Ed. Engl.*, 1996, 35, (2), 188–190

Addition reactions of Pt(PPh₃)₂ units to C₇₀ are reported, which involve the successive formation of four adducts [C₇₀{Pt(PPh₃)₂]₂, [C₇₀{Pt(PPh₃)₂]₃, [C₇₀{Pt(PPh₃)₂]₄ and [C₇₀{Pt(PPh₃)₂]₄ with the eventual addition of the four Pt atoms in a plane about the fullerene. The stepwise addition of Pt(PPh₃)₂ groups occurs first to the most pyramidalised C-C bonds at the poles of the fullerene, with subsequent additions to the adjacent 6–6 ring junctions.

Synthesis and Characterization of Platina- β -diketones

D. STEINBORN, M. GERISCH, K. MERZWEILER, K. SCHENZEL, K. PELZ, H. BÖGEL and J. MAGULL, *Organometallics*, 1996, 15, (10), 2454–2457

H₂PtCl₆ was reacted with *n*-butanol to give the but-2-ene complex H[PtCl₂(η^2 -C₄H₈)] as intermediate. This was further reacted with trimethylsilyl-substituted acetylenes R'C≡CSiMe₃ (R' = H, Me, SiMe₃) with cleavage of the silyl groups to form Pt- β -diketones [Pt₂(μ -Cl)₂{(COR)₂H}]₂, R = Me, Et.

Organopalladium and Platinum Complexes of C₆₀ Bearing Isonitrile Ligands

H. NAGASHIMA, M. NAKAZAWA, T. FURUKAWA and K. ITOH, *Chem. Lett. Jpn.*, 1996, (5), 405–406

Organo Pd or Pt complexes, (η^2 -C₆₀)M(CNR)₂, where M = Pt or Pd; R = ^tBu, 2,6-Me₂C₆H₃, 2,4,6-Me₃C₆H₂, cyclohexyl, were prepared from C₆₀M_n, where n \sim 1, and the corresponding isocyanides. Careful reaction of C₆₀Pt_n with CN(2,6-Me₂C₆H₃) yielded 72% of (η^2 -C₆₀)Pt[CN(2,6-Me₂C₆H₃)]₂. This further reacted with additional isocyanides to give (η^2 -C₆₀)Pt[CN(2,6-Me₂C₆H₃)]₃, in 77% yield.

“Swollen” Macrocycles: Palladium(II)-Directed Template Syntheses of Pendant-Arm 14-, 16-, and 18-Membered Macrocycles

M. ROSSIGNOLI, C. C. ALLEN, T. W. HAMBLEY, G. A. LAWRENCE and M. MAEDER, *Inorg. Chem.*, 1996, 35, (17), 4961–4966

Bis(diamine)Pd(II) cations with varying chain lengths undergo condensation reactions with HCHO and nitroethane to produce macromonocycles, where each pair of *cis*-disposed primary amines is converted to a -NH-CH₂-C(CH₃)(NO₂)-CH₂-NH- strap. Use of the Pd(II)-template extends the synthesis to larger ring macrocycles. Increased distortion and a change in geometric isomer occurred with increasing ring size.

Preparation and Characterization of the Dicarboxylate Cluster Complex $\text{Ru}_5(\mu_3\text{-C}_2)(\mu\text{-SMe})_2(\mu\text{-PBu}_2)_2(\text{CO})_{11}$

C. J. ADAMS and M. I. BRUCE, *Aust. J. Chem.*, 1996, 49, (4), 517–520

Bis-tertiary phosphine $\text{C}_2(\text{PBu}_2)_2(\text{dbpa})$ was prepared and used to synthesise a Ru_5 cluster containing a C_2 ligand. Pyrolysis of the Ru carbonyl derivative $\{\text{Ru}_5(\text{CO})_{11}\}_2(\mu\text{-dbpa})$ produced $\text{Ru}_5(\mu_3\text{-C}_2\text{PBu}_2)(\mu\text{-PBu}_2)(\text{CO})_{13}$ in 41% overall yield from $\text{Ru}_5(\text{CO})_{12}$. Further reaction with Me_2S_2 gave $\text{Ru}_5(\mu_3\text{-C}_2)(\mu\text{-SMe})_2(\mu\text{-PBu}_2)_2(\text{CO})_{11}$ in 19% yield.

ELECTROCHEMISTRY

Kinetics of Oxygen Reduction at IrO_2 -Coated Titanium Electrode in Alkaline Solution

C.-C. CHANG and T.-C. WEN, *J. Electrochem. Soc.*, 1996, 143, (5), 1485–1491

Cyclic voltammetry and rotating-disk electrode techniques were used to study O_2 reduction at an IrO_2 -coated Ti electrode fabricated by thermal decomposition. O_2 reduction on an electrode in alkaline solutions of pH 10.8–13.8 was catalysed by the Ir(III)/Ir(IV) transition on the IrO_2 -coated Ti electrode. In the low polarisation region, O reduction with a Tafel slope of -40 mV/decade depended on the solution pH and had a reaction order of -2 in OH^- . In the high polarisation region, the process was nearly pH independent. Both cases were first order in the dissolved O_2 concentration.

The Influence of Acetonitrile and Methanol on the Charge Transport Properties of $[\text{Os}(\text{bipy})_2(\text{PVP})_{10}\text{Cl}]\text{Cl}$ Films

D. M. KELLY and J. G. VOS, *Electrochim. Acta*, 1996, 41, (11/12), 1825–1832

Addition of acetonitrile or MeOH to aqueous LiClO_4 electrolyte solutions greatly changed the electrochemical behaviour of electrodes modified with $[\text{Os}(\text{bipy})_2(\text{PVP})_{10}\text{Cl}]\text{Cl}$ films (bipy = 2,2'-bipyridyl; PVP = poly(4-vinylpyridine)). The charge transport rate was enhanced 100-fold upon addition of 5–60% of the solvents. Polymer swelling is controlled by organic solvent content, and polymer chain motion becomes the rate limiting process, instead of ion movement.

PHOTOCONVERSION

Hydrogen Production by Water Photolysis Using Nitritoltriacetic Acid as Electron Donor

H. A. F. WERNER and R. BAUER, *J. Photochem. Photobiol., A: Chem.*, 1996, 97, (3), 171–173

H_2 was photochemically produced in a system containing $\text{Ru}(\text{bipy})_3^{2+}$, methyl viologen, colloidal Pt catalyst and nitritoltriacetic acid (NTA), as sacrificial electron donor. The highest turnover numbers were ~ 175 for both methyl viologen and $\text{Ru}(\text{bipy})_3^{2+}$, and > 250 for the Pt catalyst after 4 h irradiation at pH 4.5. Nearly 49% of NTA was oxidised after 6.5 h irradiation. The photochemical behaviours of di-(iminodiacetic) and mono-(aminoacetic) acids were also examined.

Photophysical Properties of $(\eta^2\text{-C}_{60})\text{Pd}(\text{PPh}_3)_2$ Complex in Benzene. Picosecond and Nanosecond Laser Photolysis

N. N. DENISOV, A. S. LOBACH and V. A. NADTOCHENKO, *Izv. Akad. Nauk, Ser. Khim.*, 1996, (5), 1163–1166

The spectra of photoexcited $(\eta^2\text{-C}_{60})\text{Pd}(\text{PPh}_3)_2(1)$ complexes were studied in benzene by ps and ns laser photolysis, and compared with the photoexcited C_{60} spectra and charge transfer spectra of electron donor-acceptor complexes between C_{60} and tertiary amines. The relaxation kinetics of excited (1) had three components with lifetimes $\tau_1 = 43$ ps, $\tau_2 = 1500$ ps and $\tau_3 = 1.17$ μs . The fourth level of relaxation is discussed.

Catalytic and Photocatalytic Hydrogenation of Hexanal with Molecular Hydrogen in the Presence of $\text{RhCl}(\text{PMe}_3)_2\text{CO}$

N. K. KHANNANOV, G. N. MENCHIKOVA and E. A. GRIGORYAN, *Kinet. Katal.*, 1996, 37, (1), 62–64

The Rh complex $\text{RhCl}(\text{PMe}_3)_2\text{CO}$ was found to catalyse the hydrogenation of hexanal at room temperature and H_2 pressure of > 50 atm. The reaction occurred during exposure to light of wavelength $\lambda > 340$ nm. After 4 h at room temperature, hexanol production reached 30 mole/mole of Rh.

Time-Resolved Luminescence Investigation of the Adsorption of $\text{Ru}(\text{bpy})_3^{2+}$ onto Antimony-Doped SnO_2 Colloidal Particles

W. E. FORD, J. M. WESSELS and M. A. J. RODGERS, *Langmuir*, 1996, 12, (4), 3449–3453

The adsorption of $\text{Ru}(\text{bpy})_3^{2+}$ (bpy = 2,2'-bipyridine) (1) onto negatively charged Sb-doped SnO_2 colloidal particles ~ 4 nm in diameter was monitored by time-resolved luminescence and was found to conform to the Frumkin isotherm. Electron injection from photoexcited (1) into the conduction band of the semiconductor particle resulted in luminescence quenching mainly within the laser pulse when the complex is bound to the particle, but the luminescence of the unbound complex decays with a lifetime of several hundred nanoseconds. The average maximum capacity of each particle for adsorbed (1) determined by the binding data, 29 ± 10 , is in agreement with the value obtained by ion exchange, 30 ± 4 , but is smaller than predicted for a close-packed monolayer.

trans-Chromophore-Quencher Complexes Based on Ruthenium(II)

B. J. COE, D. A. FRIESEN, D. W. THOMPSON and T. J. MEYER, *Inorg. Chem.*, 1996, 35, (16), 4575–4584

A series of chromophore-quencher complexes (1), $\text{trans-}[\text{Ru}(\text{bpy})_2(\text{py}^n)(\text{py}^m)]^{n+}$ (bpy = 2,2'-bipyridyl; py^n , py^m = substituted pyridyl ligands; $n = 2-4$) containing combinations of the electron donor PTZ in py-PTZ (py-PTZ = 10-(4-picolyl)phenothiazine) and the electron acceptors MQ^+ (1-methyl-4,4'-bipyridinium cation), etc., is described. At temperatures < 150 K the complexes display MLCT emission. At higher temperatures, visible light irradiation leads to photochemical decomposition, by crossing to a ligand-field state. This is important for the stereochemical design of Ru-based (1).

ELECTRODEPOSITION AND SURFACE COATINGS

Electroless Metal Plating on Carbonaceous Mesophase Spherules

T. TERANISHI, K. TAKEDA, Y. YAMAZAKI and M. MIYAKE, *Carbon*, 1996, 34, (5), 589–594

$\text{Pd}(\text{NH}_3)_4^{2+}$ ions (1) were immobilised electrostatically on oxidised carbonaceous mesophase spherules, M6G, at pH 11. PdCl_4^{2-} ions could not be immobilised. Ni was plated onto oxidised M6G, after immobilisation of 30 wt.% (1), at uniform thickness increasing from 0.8 to 2.0 μm , due to an increase in pH from 7–8 during plating. Cu plating was also performed.

APPARATUS AND TECHNIQUE

Double Electropolymer Modified Platinum Electrode to Follow the Kinetic Process H_2O_2 + Ascorbic Acid. Influence of the Reaction on Amperometric Biosensor Applications

I. LOSITO and C. G. ZAMBONIN, *J. Electroanal. Chem.*, 1996, 410, (2), 181–187

The kinetics of ascorbic acid (AA) oxidation by H_2O_2 was studied on a Pt electrode modified by a polypyrrole/poly(orthophenylenediamine) bilayer membrane at 27°C and pH 7. Under AA: H_2O_2 ratios of 1000:1, pseudo-first-order kinetic constant values of 3.26×10^{-3} to $4.10 \times 10^{-3}/\text{s}$ were obtained at $[\text{AA}] = 2 \text{ mM}$ and initial $[\text{H}_2\text{O}_2] = 2 \mu\text{M}$. The sensitivity and reliability of H_2O_2 detectors, with AA present, are discussed.

Enzyme Sensors Prepared by Electrodeposition on Platinized Platinum Electrodes

C. S. KIM and S. M. OH, *Electrochim. Acta*, 1996, 41, (15), 2433–2439

Platinized Pt(1)(Pt black) electrodes were used as the base electrodes for the immobilisation of glucose oxidase (GOD). The GOD sensors were made by electrodeposition of GOD/bovine serum albumin mixture on (1) and subsequent cross-linking with glutaraldehyde. The roughness factors and morphologies of the (1) surfaces depended on the platinisation potential (0 to -0.25V). Pt black electrodes plated at more negative potentials gave high current signals to the GOD sensors. Adhesion of O_2 bubbles can be greatly suppressed on the hydrophilic Pt surfaces, giving better S:N ratios in the current signals of these enzyme sensors.

Ammonia-Sensing Characteristics of Pt-Doped CdSnO_3 Semiconducting Ceramic Sensor

T. ZHANG, Y. SHEN, R. ZHANG and X. LIU, *Mater. Lett.*, 1996, 27, (4, 5), 161–164

Pt-doped mixtures of α - and β - CdSnO_3 , exhibited a high sensitivity and selectivity to NH_3 gas. Mixtures of different ratios of β : α were obtained by calcining the raw CdSnO_3 powder precursor. A 1 wt.% Pt doped mixture with β : $\alpha = 2.0$ showed a very high sensitivity and selectivity to NH_3 gas. At $\sim 240^\circ\text{C}$, the sensor can detect ppm of NH_3 in air, while at higher temperatures it can selectively detect LPG or H_2 .

Current vs Voltage Characteristics of Al- Al_2O_3 -Pd Tunnel Junction Hydrogen Sensor

S. OKUYAMA, K. OKUYAMA, N. TAKINAMI, K. MATSUSHITA and Y. KUMAGAI, *Jpn. J. Appl. Phys.*, 1996, 35, (4A), 2266–2270

The conduction mechanism of an Al- Al_2O_3 -Pd MIM (metal-insulator-metal) junction, which can operate as a H_2 gas sensor, displayed I-V characteristics that are typical of tunnelling conduction at $> 3 \text{ V}$. The barrier height of the Pd- Al_2O_3 contact obtained from the position of the logarithmic derivative maximum of the current was 3.4 eV in vacuum and decreased to 2.7 eV under 40 Pa H_2 . The barrier height of the Al- Al_2O_3 contact was 1.8 eV in vacuum and did not change with increasing H_2 pressure.

Iridium-Dispersed Carbon Paste Enzyme Electrodes

J. WANG, G. RIVAS and M. CHICHARRO, *Electroanalysis*, 1996, 8, (5), 434–437

An Ir-dispersed C-paste transducer was successful as a very selective first-generation glucose biosensor. The Ir/C particles had excellent electrocatalysis for both reduction and oxidation of H_2O_2 . This allows glucose biosensing at very low operating potentials, without interference. The Ir biocomposite had similar selectivity as its Rh and Ru counterparts and retained the sensing advantages of C paste enzyme electrodes.

Dissolved Oxygen Sensor Based on Fluorescence Quenching of Oxygen-Sensitive Ruthenium Complexes Immobilized in Sol-Gel-Derived Porous Silica Coatings

A. K. MCEVOY, C. M. MCDONAGH and B. D. MACCRAITH, *Analyst*, 1996, 121, (6), 785–788

A sensor for dissolved O based on fluorescent quenching [Ru^{II} tris(4,7-diphenyl-1,10-phenanthroline)] entrapped in a porous sol-gel SiO_2 film is reported. The sol-gel films were prepared by dip-coating onto planar and optical fibre substrates. Surface modification of the sol-gel film enhanced sensor performance. By using organically modified precursors which impart surface hydrophobicity, the quenching response can be increased by a factor > 3.5 . A very low detection limit of 6 ppb was determined for the modified films.

HETEROGENEOUS CATALYSIS

Hydrogenation of Naphthalene with Platinum-Aluminium Borate Catalysts

T.-C. HUANG and B.-C. KANG, *Chem. Eng. J.*, 1996, 63, (1), 27–36

Aluminium borate (ABx) supported Pt catalysts were studied for hydrogenation activity using naphthalene dissolved in *n*-hexadecane to simulate the aromatics in diesel fuels. The aromatic hydrogenation activity of Pt-ABx (1) was higher than that of Pt/ γ - Al_2O_3 (2), but its *cis*-decalin selectivity was lower, due to the higher acidity of the ABx support. Addition of B to (2) gave a better aromatic hydrogenation catalyst Pt-Bx- Al_2O_3 , than (1). Hydrogenation and hydrogenolysis activities of (1) increased with a decrease in the Al:B atomic ratio.

Activity of Bifunctional Pt-Dy/Al₂O₃ Catalysts in Hydrocarbon Reactions

S. CHENG, F. LI and L. LUO, *React. Kinet. Catal. Lett.*, 1996, 57, (1), 119–125

The conversions of *n*-hexane and methylcyclopentane on 0.5 wt.% Pt-Dy/Al₂O₃ containing 0.1–1 wt.% Dy were studied on catalysts prepared by co-impregnation of γ -Al₂O₃ powders with an aqueous solution of H₂PtCl₆, Dy₂O₃ and HCl. The *n*-hexane conversions over Pt-Dy/Al₂O₃ catalysts were higher than over Pt/Al₂O₃, but hydrogenolysis activity was unchanged. The dehydrocyclisation of *n*-hexane to benzene over Pt-Dy/Al₂O₃ was greater than that of Pt/Al₂O₃.

Pt-Sn/Al₂O₃ Sol-Gel Catalysts: Catalytic Properties

R. GÓMEZ, V. BERTIN, T. LÓPEZ, I. SCHIFTER and G. FERRAT, *J. Mol. Catal. A: Chem.*, 1996, 109, (1), 55–66

Pt-Sn supported catalysts, containing various amounts of Pt and Sn, were prepared by the sol-gel method by adding tetrabutyltin to a homogeneous solution containing Al tri-sec-butoxide, followed by drying, calcination and impregnation with aqueous H₂PtCl₆. The catalysts had specific BET areas of ~ 270 m²/g and Pt dispersions up to 90%, with fewer acidic sites being observed in Sn-Al₂O₃ sol-gel preparations than in sol-gel Al₂O₃. The catalysts had 54% lower selectivity to benzene formation and higher selectivity to acetone. High tolerance to thiophene poisoning during *n*-heptane dehydrocyclisation was also found.

HCN Synthesis by Ammoxidation of Methane and Ethane on Platinum Monoliths

S. S. BHARADWAJ and L. D. SCHMIDT, *Ind. Eng. Chem. Res.*, 1996, 35, (5), 1524–1533

HCN synthesis by the ammoxidation of CH₄ (1), C₂H₆ and CH₄/C₂H₆ mixtures in air or O₂ at atmospheric pressure on α -Al₂O₃ foam monoliths coated with 1–10 wt.% Pt and on Pt-10% Rh gauzes was studied. On Pt monoliths for ammoxidation of (1), HCN yields > 63% were achieved, which is comparable to yields on industrial Pt-10%Rh gauzes. Large improvements in yields were obtained by exposing the catalyst to high temperatures for several hours. Ammoxidation of C₂H₆ yielded ~42% HCN on Pt monoliths during HCN synthesis conditions. At richer C₂H₆ compositions, C₂H₄ was the dominant product.

Durability of Automotive Pd 3-Way Catalyst Added Ba or La

H. SHINJOH, T. SUZUKI, N. TAKAHASHI, K. YOKOTA, M. SUGIURA and S. MATSUURA, *Nippon Kagaku Kaishi*, 1996, (5), 433–440

The effects of adding La or Ba to a three-way Pd car catalyst were studied and compared with activities and durabilities of Pd/ γ -Al₂O₃ after ageing in simulated exhaust gases at 600–900°C. Modified catalysts had improved NO_x reduction. After ageing at > 800°C, the NO_x reduction activities of the Pd/Ba catalyst were superior to those of Pd/La under reducing conditions, and maintained high NO_x reduction, as Ba was more difficult to react with γ -Al₂O₃ than La.

Development of Supported Thin Palladium Membrane and Application to Enhancement of Propane Aromatization on Ga-Silicate Catalyst

K. KUSAKABE, S. YOKOYAMA, S. MOROOKA, J.-I. HAYASHI and H. NAGATA, *Chem. Eng. Sci.*, 1996, 51, (11), 3027–3032

A high performance thin Pd membrane was formed by Pd acetate sublimation at reduced pressure at 400°C through the macropores of an α -Al₂O₃ support tube. H₂ permeance and selectivity to N were > 10⁶ mol/m²/s/Pa and 1000, respectively. The membrane was resistant to H embrittlement and poisoning by S and Cl. Ga/SiO₂ catalyst was prepared and fitted in a tubular reactor with the Pd membrane. Propane conversion and aromatics selectivity were improved by removal of H.

Promotion Effect of Polymer-Immobilized Neodymium Ions on Catalytic Activity of Ultrafine Palladium Particles

T. TERANISHI, K. NAKATA, M. MIYAKE and N. TOSHIMA, *Chem. Lett. Jpn.*, 1996, (4), 277–278

Monodispersed ultrafine Pd particles protected by polyacrylate (PA)-Nd³⁺ complexes had catalytic activity for acrylic acid hydrogenation. The acrylic acid may be concentrated around ultrafine Pd particles by co-ordinating to Nd ions bound to the protecting polymer. A promotion effect was observed for (PA)-protected Pd particles, but not for colloidal dispersions of poly(*N*-vinyl-2-pyrrolidone)-protected particles.

Design of a Novel Pd Three-Way Catalyst: Integration of Catalytic Functions in Three Dimensions

Z. HU, C. Z. WAN, Y. K. LUI, J. DETTLING and J. J. STEGER, *Catal. Today*, 1996, 30, (1–3), 83–89

Pd catalysts for three-way conversion of HC/CO/NO were studied using simulated auto exhaust gas at 423–823 K. When CeO₂ was introduced into the Pd catalysts, NO conversion at ~ 600 K was reduced, while NO conversion at ~ 770 K increased. An integrated Pd-only catalyst washcoat was designed, consisting of a top Pd and a bottom Pd-Ce layer, to maximise HC/CO/NO performance. Engine and vehicle evaluation showed that this catalyst, which integrates Pd sites and O₂ storage components in three dimensions, has superior three-way performance.

Synthesis of Ru, Rh and Pd Complexes Immobilized on Modified Supports. Investigation of the Hydrogenation of Cinnamaldehyde

V. ISAEVA, A. DEROUAULT and J. BARRAULT, *Bull. Soc. Chim. Fr.*, 1996, 133, (4), 351–357

Cinnamaldehyde was hydrogenated over complexes, such as Rh₂(O₂CCH₃)₄ (1), Ru₂(O₂CCH₃)₄ (2), Pd(NH₃)₄Cl₂, PdCl₂ or Ru₂(O₂CCH₃)₄, immobilised on modified supports, such as SiO₂ gels or resins. The selectivity to unsaturated alcohol was improved by using weak base supports containing aliphatic or heterocyclic amino groups; immobilised (2) was the best. Immobilised (1) catalysed C=C bond hydrogenation.

CO₂ Hydrogenation to Ethanol over Promoted Rh/SiO₂ Catalysts

H. KUSAMA, K. OKABE, K. SAYAMA and H. ARAKAWA, *Catal. Today*, 1996, 28, (3), 261–266

Hydrogenation of CO₂ to EtOH was performed over Rh/SiO₂ based catalysts promoted with various metal oxides; Li salts had the most prominent effect on EtOH formation. Under optimised reaction conditions, the highest EtOH selectivity obtained over Rh-Li/SiO₂ was 15.5% with a CO₂ conversion of 7.0% at 5 MPa and 513 K in a flow of H₂-CO₂ premixed gas with a flow-rate of 100 cm³/min. In-situ FT-IR studies suggest that CO₂ was hydrogenated to EtOH via CO intermediate(s).

Catalytic Activity of Perovskite-Type La_{0.8}Sr_{0.2}M₁₋₂Cu_{0.1}Ru_{0.1}O₃ (M = Al, Mn, Fe, Co) for CO Oxidation and NO-CO Reactions. Influence of the Simultaneous Substitution of Cu and Ru

Y. TERAOKA, H. NII, S. KAGAWA, K. JANSSON and M. NYGREN, *Chem. Lett. Jpn.*, 1996, (4), 323–324

The catalytic activity of the ABO₃ perovskite-type title compound for CO oxidation and NO-CO reactions was greatly changed by the simultaneous substitution of Cu and Ru for M at the B sites. The effect was dependent on the host M cations. The simultaneous incorporation of Cu and Ru gave a very active catalyst La_{0.8}Sr_{0.2}Al_{0.8}Cu_{0.1}Ru_{0.1}O₃ (1) for both CO-NO and CO-O₂ reactions, at a substitution level (y-value) of 0.1. The activity of (1) was comparable to that of 0.5 wt.% Pt/Al₂O₃ or La_{0.8}Sr_{0.2}CoO₃, which is one of the most active perovskite catalysts.

HOMOGENEOUS CATALYSIS

An Improved Synthesis of 1,4-*cis,exo*-Hexa- or Tetrahydromethano- or -ethanobiphenylene Derivatives Catalyzed by Palladium Complexes

M. CATELLANI and L. FERLIOLI, *Synthesis*, 1996, (6), 769–772

A direct method for the preparation of *exo*-disubstituted benzocyclobutenes based on the use of K₂CO₃ in DMF in the presence of Pd(PPh₃)₄ catalyst is reported. The reaction, performed at 105°C for 12–24 h, with a Pd(PPh₃)₄:substrate:K₂CO₃ molar ratio = 1:20:24 gave good to excellent yields, particularly when *ortho*-substituents were present in the aromatic ring. The *exo* orientation of the cycloaliphatic substituents on the cyclobutene ring was confirmed by ¹H and ¹³C NMR spectroscopic measurements.

Allylic Alkylation with a Supported Aqueous Phase Palladium Catalyst

P. SCHNEIDER, F. QUIGNARD, A. CHOPLIN and D. SINOUE, *New J. Chem.*, 1996, 20, (5), 545–547

The allylic alkylation of (*E*)-cinnamyl ethyl carbonate was catalysed by SiO₂ supported aqueous phase Pd/tpts, where tpts is P(C₆H₄-*m*-SO₃Na)₃. The water soluble catalyst was prepared in situ from Pd(OAc)₂ and tpts. The stability of the complex and the absence of metal leaching allowed easy catalyst recycling.

Highly Stereoselective Palladium-Catalyzed Coupling Reactions of Captodative Olefins Acetylvinyln Arenecarboxylates

L. VILLAR, J. P. BULLOCK, M. M. KHAN, A. NAGARAJAN, R. W. BATES, S. G. BOTT, G. ZEPEDA, F. DELGADO and J. TAMARIZ, *J. Organomet. Chem.*, 1996, 517, (1–2), 9–17

The reaction of the captodative olefin 3-(*p*-nitrobenzoyloxy)-3-buten-2-one with aryl and vinyl halides was catalysed by (Ph₃P)₂PdCl₂ to give coupled products 4-aryl- and 4-vinyl-3-(*p*-nitrobenzoyloxy)-3-buten-2-ones, respectively, with high *Z* stereoselectivity. Catalytic cross-coupling alkylation, phenylation and vinylation with trialkylorganostannanes and bromo olefin (*Z*)-4-bromo-3-(*p*-nitrobenzoyloxy)-3-buten-2-one) gave the corresponding trisubstituted alkenes.

Transition Metal Complexes of Diazenes XXXVI. [1a]: Formation of Indoles from Azobenzene and Diphenylacetylene through Supported Aqueous Phase Catalysis by Rhodium(I) Complexes

S. WESTERNACHER and H. KISCH, *Monash. Chem.*, 1996, 127, (5), 469–473

The addition of diphenylacetylene to azobenzene was catalysed by Rh(I) trisulphonated triphenylphosphine supported on SiO₂, in refluxing butanol in the presence of triphenylphosphine to give *N*-anilino-2,3-diphenylindole and 2,3-diphenylindole with turnover numbers of 80 and 20, respectively. This supported aqueous phase system retained a constant turnover frequency throughout the reaction and could be partially recycled.

Rhodium-Catalyzed Carbonylation of 2-Alkynylbenzaldehyde under Water-Gas Shift Reaction Conditions: Formation of Novel Tricyclic Lactones

T. SUGIOKA, S.-W. ZHANG, N. MORII, T. JOH and S. TAKAHASHI, *Chem. Lett. Jpn.*, 1996, (4), 249–250

A tricyclic lactone was prepared by the carbonylation of 2-alkynylbenzaldehyde under water-gas shift reaction conditions in the presence of Rh₂(CO)₄ in a chloroform solvent. The lactone was the major product with ≤ 59% yield. The reactions of 2-phenylethynylbenzaldehyde derivatives with a substituent at the 4-position of the phenyl group gave the corresponding tricyclic products in 54% and 44% yields.

Hydrogenation of Organic Substrates by Isocyanide Polymer-Bound Rh(PPh₃)₃Cl

R. GIANNANDREA, P. MASTRORILLI, G. ZACCARIA and C. F. NOBILE, *J. Mol. Catal. A: Chem.*, 1996, 109, (2), 113–117

Isocyanide polymer-bound Rh(PPh₃)₃Cl was prepared by quantitative co-ordination to hydrophilic macromolecular isocyanides. The organic support was obtained by copolymerisation of 3-isocyanopropyl acrylate with oxytriethylene glycol methacrylate, in the presence of triethylene glycol dimethacrylate as cross-linker. At 50°C under 1 atm H₂, the complex became a versatile and recyclable catalyst for the hydrogenation of alkenes, alkynes, nitriles and nitrocompounds.

Ruthenium-Catalyzed Allylic Substitution of Allylic Cyclic Carbonates

S.-K. KANG, D.-Y. KIM, R.-K. HONG and P.-S. HO, *Synth. Commun.*, 1996, 26, (17), 3225–3235

(E)-Allylic alcohol and erythro- β -hydroxy thiophenoxide or phenoxide were prepared by allylic substitution of allylic cyclic carbonates with PhSH or PhOH, respectively, in the presence of CpRu(PPh₃)₂Cl (5 mol%), via external attack of nucleophiles to π -allyl Ru complex. For the methyl-substituted allylic cyclic carbonate, only β -hydroxy sulphide was obtained after refluxing for 48 h, which indicated that the substitution reaction was very sensitive to steric effects.

Ruthenium-Catalyzed *cis*-Dihydroxylation of Alkenes: Scope and Limitations

T. K. M. SHING, E. K. W. TAM, V. W.-F. TAI, I. H. F. CHUNG and Q. JIANG, *Chem. Eur. J.*, 1996, 2, (1), 50–57

Oxidative Ru-catalysed dihydroxylation of a wide range of alkenes with EtOAc or CCl₄, acetonitrile, and H₂O in the ratio 3:3:1, or with acetonitrile and H₂O in the ratio 6:1 in the presence of 0.07 mol equiv. of RuCl₃(H₂O)₃ and 1.5 mol. equiv. of NaIO₄, at 0–5°C gave *syn*-diols rapidly and efficiently. With substrates containing electron-withdrawing group(s), the reactions were slower but gave better yields. Cyclohexene derivatives had better diastereoselectivities for *syn*-dihydroxylation *anti* to the existing α -stereogenic centre than acyclic alkenes.

Catalytic Activities of New Arsine-Dihydrido Ruthenium(II) Complexes in the Homogeneous Hydrogenation of Aldehyde

J.-Y. KIM, M.-J. JUN and W.-Y. LEE, *Polyhedron*, 1996, 15, (21), 3787–3793

A number of arsine-dihydrido Ru(II) complexes, [RuH₂(CO)(AsPh₃)₃] (1) and [RuH₂(CO)(AsPh₃)(L-L)], where L-L = diars (2), arphos (3), diphos (4), were prepared. Their catalytic activities for the hydrogenation of propionaldehyde to yield propan-1-ol were studied at 130°C and 30 atm H₂, and compared with the catalytic activity of [RuH₂(CO)(PPh₃)₃] (5). Complexes with a chelate ring had higher catalytic activities than (1). The catalytic activities decreased in the order: (4) > (3) > (2) > (5) > (1).

FUEL CELLS

Development and Electrochemical Studies of Gas Diffusion Electrodes for Polymer Electrolyte Fuel Cells

V. A. PAGANIN, E. A. TICIANELLI and E. R. GONZALEZ, *J. Appl. Electrochem.*, 1996, 26, (3), 297–304

Low catalyst loading gas diffusion electrodes for polymer electrolyte fuel cells were studied electrochemically. The best performance was obtained with an electrode formed from 20 wt.% Pt/C, 0.4 mg Pt/cm² and 1.1 mg Nafion[®]/cm² in the catalyst layer and 15% PTFE in a 50 μ m thick diffusion layer. Optimum operating conditions for PEFC occurred at a cell temperature of 80°C and H and O/air humidifiers at 15 and 5°C above the cell temperature, respectively.

Conversion of Methane to Synthesis Gas over Pt Electrode in a Cell with Solid Oxide Electrolyte

V. V. GAL'VITA, V. D. BELYAEV, V. N. PARMON and V. A. SOBYANIN, *Catal. Lett.*, 1996, 39, (3, 4), 209–211

Electrochemical oxidation of CH₄ to syngas was studied over a Pt electrode-catalyst in a SOFC at 800°C with a solid oxygen conducting electrolyte, such as yttria stabilised zirconia (YSZ). The Pt electrode was found to be active for the partial oxidation of CH₄ to syngas. CO selectivity and yields of 85 and 65%, respectively, were obtained. The Pt electrodes, porous and of thickness ~ 10 μ m, were prepared by calcination of a Pt paste, containing 5 wt.% of YSZ in air at 950°C. For stable electrochemical characteristics, the electrodes were pretreated with both the anodic and cathodic current in air at 850°C for 20 h.

ELECTRICAL AND ELECTRONIC ENGINEERING

Electroplated, High H_c CoPt Films: δM Magneto-Optical Measurements

L. CALLEGARO, E. PUPPIN, P. L. CAVALLOTTI and G. ZANGARI, *J. Magn. Magn. Mater.*, 1996, 155, (1–3), 190–192

Co-rich CoPt and CoPtP alloy thin films were obtained by electrodeposition. Adding a P compound to the electrolyte for CoPt deposition resulted in P codeposition and improved the hard magnetic properties of the film, giving coercive forces \leq 5500 Oe. δM curves, to characterise interactions in ferromagnetic material, revealed exchange coupling in CoPt, but mainly magnetostatic interactions in CoPtP films.

Excellent Au/Ge/Pd Ohmic Contacts to n-Type GaAs Using Mo/Ti as the Diffusion Barrier

C.-Y. CHAI, J.-A. HUANG, Y.-L. LAI, J.-W. WU, C.-Y. CHANG, Y.-J. CHAN and H.-C. CHENG, *Jpn. J. Appl. Phys.*, 1996, 35, (4A), 2110–2111

The Au/Ge/Pd ohmic metallisation system on n-type GaAs is significantly improved by using an additional Mo/Ti bi-layer as the diffusion barrier. Optimum conditions were achieved in the annealing temperature range of 325–400°C for 60 s. The minimum specific contact resistivity achievable was $1.2 \times 10^{-7} \Omega \text{ cm}^2$. The improvements are attributed to the effective retardation of As-outdiffusion by the Mo/Ti barrier.

Ohmic Contacts to n-Type GaN Using Pd/Al Metallization

A. T. PING, M. ASIF KHAN and I. ADESIDA, *J. Electron. Mater.*, 1996, 25, (5), 819–824

Ohmic contacts to n-type GaN grown by metalorganic CVD were formed using a Pd/Al based metallisation. As-deposited Pd/Al produced rectifying contacts while subsequent annealing at \geq 400°C produced ohmic contacts; contact resistance decreased with decreasing Pd interlayer thickness. A minimum contact resistance and specific contact resistance of 0.9 $\Omega \text{ mm}$ and $1.2 \times 10^{-3} \Omega \text{ cm}^2$, respectively, were obtained after rapid thermal annealing at 650°C for 30 s.