

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Novel Carbon Supported Material: Highly Dispersed Platinum Particles on Carbon Nanospheres

P. SERP, R. FEURER, Y. KIHN, P. KALCK, J. L. FARIA and J. L. FIGUEIREDO, *J. Mater. Chem.*, 2001, 11, (8), 1980–1981

Highly dispersed Pt nanoparticles (3–6 nm) were deposited by low temperature CVD of $[\text{PtMe}_2(\eta^4\text{-C}_6\text{H}_{12})]$ in a fluidised bed reactor on C nanospheres of low surface area. Nitric acid oxidative treatment was used to increase the concentration of grafting sites on the C. The precursor was sublimed at 343 K and decomposed at 383 K in the presence of small amounts of H_2 added to the He carrier gas at 1316 Pa. This new Pt material may have catalytic and electrochemical applications.

Synthesis of Palladium Nanoparticles in Water-in-Oil Microemulsions

C.-C. WANG, D.-H. CHEN and T.-C. HUANG, *Colloids Surf. A: Physicochem. Eng. Aspects*, 2001, 189, (1–3), 145–154

Pd nanoparticles can be synthesised by the reduction of $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ with hydrazine in cationic H_2O -in-oil microemulsions of H_2O /cetyl-trimethylammonium bromide, *n*-butanol/isooctane at 25°C. The Pd nanoparticles are crystalline with a f.c.c. structure. Their magnetic susceptibility was significantly higher than that of bulk Pd.

An Investigation of the Partial Phase Diagrams of Ag-Pd-Gd-20Ru and Ag-Pd-Gd-50Ru Quaternary Systems

K. ZHANG, Y. XU and Q. LI, *Precious Met. (Chin.)*, 2001, 22, (4), 1–6

The phase diagrams of the Ag-Pd-Ru-rich side (Gd < 25 at.%) in the Ag-Pd-Ru-Gd quaternary system were studied by XRD, SEM and optical microscopy. Isothermal sections at 700°C of Ag-Pd-Gd-20Ru and Ag-Pd-Gd-50Ru were determined. Both sections contained three two-phase regions: Pd(Ag) + (Ru), (Ru) + $\text{Ag}_5\text{Gd}_{14}$ and (Ru) + Pd₃Gd; three three-phase regions: Pd(Ag) + Pd₃Gd + (Ru), Pd(Ag) + $\text{Ag}_5\text{Gd}_{14}$ + (Ru) and Pd₃Gd + $\text{Ag}_5\text{Gd}_{14}$ + (Ru); and one four-phase region: Pd(Ag) + Pd₃Gd + $\text{Ag}_5\text{Gd}_{14}$ + (Ru).

Ternary Al-Pd-Co Monoclinic Phases

S. MI, M. YURECHKO, J. WU and B. GRUSHKO, *J. Alloys Compd.*, 2001, 329, (1–2), L1–L4

The ternary Al-Pd-Co V-phase and U-phase were investigated using powder X-ray and electron diffraction. The V-phase has a primitive structure with $a = 1.0068(2)$ nm, $b = 0.3755(1)$ nm, $c = 0.6512(4)$ nm and $\beta = 102.38(6)^\circ$ for $\text{Al}_{70.0}\text{Pd}_{9.2}\text{Co}_{20.8}$. The U-phase has a C-centred monoclinic structure with $a = 1.9024(4)$ nm, $b = 2.9000(4)$ nm, $c = 1.3140(4)$ nm and $\beta = 117.26(3)^\circ$ for $\text{Al}_{69.1}\text{Pd}_{16.5}\text{Co}_{14.4}$.

Microstructure Characterization of Ceramic Composites Formed by Controlled Melt Oxidation of Al-Mg-Pd Alloys

M. PINKAS, N. FRAGE, E. MANOR and A. VENKERT, *J. Mater. Sci.*, 2001, 36, (14), 3525–3529

Ceramic matrix composites were formed by controlled melt oxidation of $\text{Al}_{98-x}\text{Mg}_2\text{Pd}_x$ ($x = 0.5, 1.5$ and 3 at.%) alloys. The Pd addition was found to increase the growth rate, the metal volume fraction, the diameter of the metal channels and promote the formation of a uniform microstructure.

Transition from Nucleation Controlled to Growth Controlled Crystallization in $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$ Melts

J. SCHROERS, Y. WU, R. BUSCH and W. L. JOHNSON, *Acta Mater.*, 2001, 49, (14), 2773–2781

Crystallisation of undercooled $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$ melts was studied under isothermal conditions in a differential scanning calorimeter. The results are summarised in a time-temperature-transformation (TTT) diagram which shows two time scales. One is the time to reach 1% of crystallised volume fraction and reflects the typical 'nose' shape of the TTT diagram. The other is the width of the crystallisation event itself, which increases with decreasing temperature from 90 s at 793 K to 10,200 s at 623 K.

CHEMICAL COMPOUNDS

Linkage of Heteronuclear Rhodium-Platinum Clusters

I. O. KOSHEVOY, S. P. TUNIK, S. JÄÄSKELÄINEN, M. HAUKKA and T. A. PAKKANEN, *J. Chem. Soc., Dalton Trans.*, 2001, (20), 2965–2967

$[\text{PtCl}(\text{dppm})]_2$ and $[\text{Pt}_2(\text{CO})_3(\text{dppm})_2]$ react with $[\text{Rh}_6(\text{CO})_{15}]^{2-}$ and $[\text{Rh}_6(\text{CO})_{15}(\text{NCMe})]$, to give as the main products, $[\text{Rh}_6\text{Pt}_2(\text{CO})_{21}(\text{dppm})_2]$ (1) and $[\text{Rh}_6\text{Pt}_4(\text{CO})_{16}(\text{dppm})_3]$ (2), respectively. The mixed metal Rh_2Pt_2 cluster in (1) and the tetranuclear Pt_4 cluster in (2) are bonded to the Rh_6 metal core via Rh–Rh and Pt–Rh bonds.

Pincer-Like Amido Complexes of Platinum, Palladium, and Nickel

J. C. PETERS, S. B. HARKINS, S. D. BROWN and M. W. DAY, *Inorg. Chem.*, 2001, 40, (20), 5083–5091

Bis(8-quinoliny)amine (1) (BQAH), (2-pyridin-2-yl-ethyl)-(8-quinoliny)amine (2), *o*-dimethylamino-phenyl(8-quinoliny)amine (3) and 3,5-dimethyl-phenyl(8-quinoliny)amine (4) were prepared from aryl halide and amine precursors by Pd-catalysed coupling reactions. From (1), (BQA)PtCl, (BQA)PdCl and (BQA)NiCl were then prepared. While reaction of (2) gave a product mixture, (3) and (4) reacted with (COD)PtCl₂ to afford coordinated cyclic dienes.

New Linked Macrocyclic Systems. Interaction of Palladium(II) and Platinum(II) with Tri-Linked N₂S₂-Donor Macrocycles and Their Single-Ring Analogues

I. M. ATKINSON, J. D. CHARTRES, A. M. GROTH, L. F. LINDOY, M. P. LOWE, G. V. MEEHAN, B. W. SKELTON and A. H. WHITE, *J. Chem. Soc., Dalton Trans.*, 2001, (19), 2801–2806

[M₃L](PF₆)₆ (1) (M = Pt, Pd; L = ligand incorporating three linked, 16-membered, N₂S₂-donor macrocycles having a 1,3,5-'tribenzyl' or a phloroglucinol core), together with their single-ring analogues were synthesised. Electrospray MS of (1) gives a series of multiply charged ions resulting from the loss of hexafluorophosphate counter ions and hydrogens: [M - nPF₆]ⁿ⁺ and [M - nPF₆ - mH]^{(n-m)+}.

A New Molecular Metal Based on Pd(dmit)₂: Synthesis, Structure and Electrical Properties of (C₇H₁₃NH)[Pd(dmit)₂]₂ (dmit²⁻ = 2-thioxo-1,3-dithiole-4,5-dithiolate)

T. NAITO, T. INABE, H. KOBAYASHI and A. KOBAYASHI, *J. Mater. Chem.*, 2001, 11, (9), 2199–2204

Air-oxidation of an acetone-acetic acid solution of (C₇H₁₃NH)₂[Pd(dmit)₂] gave black shiny platelets of (C₇H₁₃NH)[Pd(dmit)₂]₂ (1). (1) has a criss-cross columnar structure. Although (C₇H₁₃NH)⁺ is orientationally disordered on a 2-fold axis, (1) exhibited metallic conductivity down to ~ 40 K. The room temperature conductivity is ~ 22 S cm⁻¹ and the resistivity decreased with decreasing temperature.

PHOTOCONVERSION

Luminescence and Photocatalytic Properties of a Platinum(II)-Quaterpyridine Complex Incorporated in Nafion Membrane

X.-H. LI, L.-Z. WU, L.-P. ZHANG, C.-H. TUNG and C.-M. CHE, *Chem. Commun.*, 2001, (21), 2280–2281

Non-emissive [Pt(2,2':6',2'':6''-quaterpyridine)]-(CF₃SO₃)₂ (1) incorporated in Nafion membrane exhibits strong photoluminescence at room temperature. The rigid matrix of Nafion stabilises (1) towards photochemical decomposition even in the presence of O₂. This system can be used as a sensitiser to generate singlet O to oxidise alkenes.

Photoreaction of Platinum(II) β-Diketonate Complexes with Olefins

F. WANG, X. WU, A. A. PINKERTON, P. KUMARADHAS and D. C. NECKERS, *Inorg. Chem.*, 2001, 40, (23), 6000–6003

Pt(hfac)₂ (hfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato) reacted with C₂H₄ when irradiated at 350 nm to give Pt(hfac)₂(η²-C₂H₄). When Pt(hfac)₂ and C₂H₄ were irradiated at 300 nm, a second product, that was non-isolable, was detected by ¹H and ¹⁹F NMR. Pt(hfac)₂(η²-C₂H₄) is not stable at shorter wavelengths. The photoproducts of Pt(hfac)₂ with C₃H₆ and of Pt(tfac)₂ (tfac = 1,1,1-trifluoro-2,4-pentanedionato) with C₂H₄ were detected by ¹H NMR.

Photoenhanced Reduction of CO₂ by H₂ over Rh/TiO₂ Characterization of Supported Rh Species by Means of Infrared and X-Ray Absorption Spectroscopy

Y. KOHNO, T. YAMAMOTO, T. TANAKA and T. FUNABIKI, *J. Mol. Catal. A: Chem.*, 2001, 175, (1–2), 173–178

IR study of the photoenhanced reduction of CO₂ by H₂ in the presence of Rh/TiO₂ (1) showed adsorbed CO arose even on strongly reduced (1). IR and X-ray absorption studies showed a decrease in the Rh particle size with prolonged photoreaction and decreased electron transfer from (1) to adsorbates.

Surfactant Chain Length Effects on the Light Emission of Tris(2,2'-bipyridyl)ruthenium(II)/Tripropylamine Electrogenerated Chemiluminescence

B. FACTOR, B. MUEGGE, S. WORKMAN, E. BOLTON, J. BOS and M. M. RICHTER, *Anal. Chem.*, 2001, 73, (19), 4621–4624

The anodic oxidation of Ru(bpy)₃²⁺ produces electrochemiluminescence (ECL) in the presence of tri-*n*-propylamine (TPrA) in aqueous nonionic surfactant solution. Increases in ECL efficiency (≥ 5 fold) and TPrA oxidation current (≥ 2 fold) were observed. Slight decrease in ECL intensity was observed with increase of surfactant chain length.

ELECTRODEPOSITION AND SURFACE COATINGS

Electrochemical Deposition of Fine Pt Particles on n-Si Electrodes for Efficient Photoelectrochemical Solar Cells

S. YAE, M. KITAGAKI, T. HAGIHARA, Y. MIYOSHI, H. MATSUDA, B. A. PARKINSON and Y. NAKATO, *Electrochim. Acta*, 2001, 47, (1–2), 345–352

Electrochemical deposition of fine Pt particles on n-Si electrodes (1) from an aqueous H₂PtCl₆ solution was carried out by the single- (SPS) and double-potential step (DPS) methods. The distribution density of the Pt particles was 10⁸ cm⁻² for SPS but increased from 10⁹ to 10¹⁰ cm⁻² by a shift of the pulse potential at the initial step of DPS from -1.0 to -4.0 V vs. SCE. Photoelectrochemical solar cells with (1) generated open-circuit photovoltages of 0.51–0.61 V, which is higher than those for n-Si electrodes coated with continuous Pt layers (~ 0.2–0.3 V).

Highly (111)-Oriented and Conformal Iridium Films by Liquid Source Metalorganic Chemical Vapor Deposition

J. GOSWAMI, C.-G. WANG, P. MAJHI, Y.-W. SHIN and S. K. DEY, *J. Mater. Res.*, 2001, 16, (8), 2192–2195

The title Ir films were deposited by a liquid source MOCVD process. The O₂-assisted pyrolysis of CH₃CpIrCOD yielded Ir films at substrate temperatures, T_{sub}, of 300–700°C. With increasing T_{sub}, the (111) orientation increased, and at T_{sub} = 700°C, the I₁₁₁/I₂₀₀ ratios were as high as 186 and 277 for amorphous SiO₂ and native SiO₂ surfaces, respectively.

APPARATUS AND TECHNIQUE

Continuous Detection of Volatile Aromatic, Unsaturated or Halogenated Hydrocarbons in Air by Adsorption on Pt-Electrodes and Subsequent Oxidative Desorption

S. ERNST, R. HERBER, E. SLAVCHEVA, I. VOGEL and H. BALTRUSCHAT, *Electroanalysis*, 2001, 13, (14), 1191–1197

Benzene, its derivatives and simple halogenated hydrocarbons can be detected by means of their adsorption at a Pt sensor electrode. The charge is automatically determined during a subsequent sweep to potentials above 1 V (RHE). It is corrected for O₂ adsorption and serves as a measure for the substance concentration. A special potential program repeatedly strips the adsorbate from the surface.

Solid Polyelectrolyte (SPE) Membranes Containing a Textured Platinum Catalyst

D. G. BESSARABOV and W. C. MICHAELS, *J. Membrane Sci.*, 2001, 194, (1), 135–140

Perfluorinated cation-exchange flat-sheet membranes were treated with CH₃(CH₂)₁₅N(CH₃)₃Br surfactant. The electroless chemical deposition of a Pt catalyst on the modified membranes was achieved by means of the Takenaka-Torikai method. The Pt particles were small in size and pyramidally textured.

Stationary-State Oxidized Platinum Microsensor for Selective and On-Line Monitoring of Nitric Oxide in Biological Preparations

A. CSEREY and M. GRATZL, *Anal. Chem.*, 2001, 73, (16), 3965–3974

A simple electrochemical NO sensor uses a glass sealed Pt microdisk electrode coated with cellulose acetate to reduce both surface fouling by proteins and its response to potential interferences. The electrode utilises NO oxidation with differential pulse amperometry. The oxidation of NO by O₂ was found to be second order in [NO] with a rate constant of $(8 \pm 0.4) \times 10^6 \text{ M}^{-2} \text{ s}^{-1}$. Chemical generation of NO by ascorbic acid provides accurate means of calibration and a way for *in vivo* stimulations.

A Reagentless Glucose Biosensor Based on Glucose Oxidase Entrapped into Osmium-Complex Modified Polypyrrole Films

S. REITER, K. HABERMÜLLER and W. SCHUHMAN, *Sens. Actuators B, Chem.*, 2001, 79, (2–3), 150–156

The title sensor is formed by entrapment of glucose oxidase within an electrochemically generated copolymer of an Os-complex substituted pyrrole derivative and pyrrole (1). By employing glassy C as electrode material, the electron transfer pathway from the enzyme via the polymer-bound (1) to the electrode could be proven even in the presence of traces of O₂. Enhancement of the glucose-dependent current was achieved by increasing the hydrophilicity of the polymer film and introduction of carboxylic acid side chains at the polypyrrole backbone.

HETEROGENEOUS CATALYSIS

Kinetics of the CO + O₂ Reaction over Three-Way Pt-Rh Catalysts

P. GRANGER, J. J. LECOMTE, L. LECLERCQ and G. LECLERCQ, *Appl. Catal. A: Gen.*, 2001, 218, (1–2), 257–267

The kinetics of the reaction between CO and O₂ over Pt-Rh/Al₂O₃ was studied using a differential fixed bed flow reactor under reducing conditions (CO:O₂ > 5). Temperature, CO and O₂ partial pressures were 25–500°C, $(5–9) \times 10^{-3}$ and $(0.25–2) \times 10^{-3}$ atm, respectively. A bimolecular reaction between adsorbed CO and adsorbed O₂ molecules is seen as the determining step. CO is adsorbed much more strongly than O₂ under the experimental conditions employed.

Effect of the Solvent Used during Preparation on the Properties of Pt/Al₂O₃ and Pt-Sn/Al₂O₃ Catalysts

L. S. CARVALHO, P. REYES, G. PECCHI, N. FIGOLI, C. L. PIECK and M. DO CARMO RANGEL, *Ind. Eng. Chem. Res.*, 2001, 40, (23), 5557–5563

The effect of H₂O, acetone or EtOH used during Al₂O₃ impregnation in the preparation of the title catalysts produced catalysts with different properties and performances in *n*-pentane isomerisation, cyclohexane dehydrogenation and *n*-octane reforming. The catalysts prepared in EtOH had the highest metallic dispersion. Pt/Al₂O₃ (acetone) had the highest activity for isomerisation while the activity of Pt-Sn/Al₂O₃ catalysts was: EtOH > acetone > H₂O.

A Novel, Highly Efficient Catalyst for Propane Dehydrogenation

D. AKPORIAYE, S. F. JENSEN, U. OLSBYE, F. ROHR, E. RYTTER, M. RØNNEKLEIV and A. I. SPJELKAVIK, *Ind. Eng. Chem. Res.*, 2001, 40, (22), 4741–4748

Pt₄Sn/Mg(Al)O (from calcined hydrotalcite) is a new and highly efficient catalyst for the dehydrogenation of propane. It is superior to conventional Al₂O₃-supported systems in terms of lifetime stability, activity and propene selectivity. Impregnation of the calcined hydrotalcite in aqueous solution (or HCl-acidified aqueous solution followed by Cl removal) yields catalyst with better long-term stability than catalyst prepared in EtOH solution.

Selective Transfer Dehydrogenation of Aromatic Alcohols on Supported Palladium

C. KERESZEGI, T. MALLAT and A. BAIKER, *New J. Chem.*, 2001, 25, (9), 1163–1167

Transfer dehydrogenation of alcohols has been investigated over Pd/support systems using olefins as hydrogen acceptors. Pd/Al₂O₃ with cyclohexene is the most active and selective system and allows facile and convenient synthesis of aromatic ketones. Hydrogenolysis-type side reactions can be minimised by minute additions of a tertiary amine (selective poisoning of Pd), such as Et₃N. The low reactivity of aliphatic and cycloaliphatic alcohols can be utilised for the selective synthesis of aromatic ketones.

Reduction of Nitrogen Oxides over Unsupported Iridium: Effect of Reducing Agent

C. WÖGERBAUER, M. MACIEJEWSKI and A. BAIKER, *Appl. Catal. B: Environ.*, 2001, 34, (1), 11–27

Propene, propane, CO and H₂ were used as reducing agents in the selective reduction of NO_x (NO or NO₂) over Ir black, in the presence and absence of O₂. Only propene exhibits appreciable activity for the reduction of NO under oxidising conditions. In O₂-free atmospheres under large excess of the reducing agent, with propene considerable amounts of HCN were formed and with H₂ the major product was NH₃. The presence of NO_x shifts propene oxidation light-off to higher temperatures.

Kinetic Study of CO₂ Reforming of Propane over Ru/Al₂O₃

D. SUTTON, J.-F. MOISAN and J. R. H. ROSS, *Catal. Lett.*, 2001, 75, (3–4), 175–181

The rate of reaction of C₃H₈ over Ru/Al₂O₃ was determined as a function of the partial pressures of the reactants, C₃H₈ and CO₂ at 600 and 650°C. The order of the reaction was 0.3 with respect to CO₂, indicating its involvement in the rate determining step of the reaction. The order of reaction was 0 in C₃H₈. The activation energy of C₃H₈ was calculated as 86 kJ mol⁻¹. The activation energies for the formation of H₂ and CO were calculated as 80 and 66 kJ mol⁻¹, respectively. There was a decrease in the CO:H₂ ratio with an increase in temperature.

HOMOGENEOUS CATALYSIS

Palladium(II)- and Rhodium(III)-Catalyzed

Carbonylation Reaction of Aryltin Compounds

T. OHE, S. MOTOFUSA, K. OHE and S. UEMURA, *Bull. Chem. Soc. Jpn.*, 2001, 74, (7), 1343–1348

Aryltin compounds can be employed for carbonylation reactions in the presence of a catalytic amount of Pd(II) salt, with reoxidant, such as CuCl₂, in MeCN or AcOH under an atmospheric pressure of CO to give arenecarboxylic acids and diaryl ketones. Rh(III) salts can also be used and reoxidant is sometimes not necessary. More than one of two, three or four aryl groups of the aryltin compounds can be transferred to the products in this catalytic carbonylation.

Palladium-Catalyzed Cyclization of Allylsilanes with Nucleophilic Displacement of the Silyl Group

I. MACSÁRI and K. J. SZABÓ, *Chem. Eur. J.*, 2001, 7, (19), 4097–4106

Allylsilanes with hydroxy or tosylamide groups undergo Pd(II)-catalyzed cyclisation to give derivatives of tetrahydrofuran, piperidine and pyrrolidine through an (η^3 -allyl)Pd (1) intermediate, which is generated by allylic displacement of the silyl group of the allylsilane precursors. Benzoquinone and Cu(II) chloride can be used for regeneration of the Pd(II) catalyst precursor. The reaction rate for the formation of (1) is highly dependent on the concentration of the chloride ligand and of the solvent.

A New Practical Ketone Synthesis Directly from Carboxylic Acids: First Application of Coupling Reagents in Palladium Catalysis

L. J. GOOBEN and K. GHOSH, *Chem. Commun.*, 2001, (20), 2084–2085

A Pd-catalysed cross-coupling reaction between arylboronic acids and carboxylic acids, activated *in situ* for the oxidative addition to a tricyclohexylphosphine Pd(0) catalyst by treatment with di(*N*-succinimidyl) carbonate was demonstrated. A high yielding synthesis of various functionalised arylketones under mild conditions was achieved. THF was the most effective solvent and an addition of Na₂CO₃ base enhanced the stability of the catalytic system.

Palladium-Catalyzed Arylation of Allylic Alcohols with Aryl Iodides in Water

H. ZHAO, M.-Z. CAI, R.-H. HU and C.-S. SONG, *Synth. Commun.*, 2001, 31, (23), 3665–3669

Pd-catalysed arylation of allylic alcohols with aryl iodides occurs in the presence of NaHCO₃ and Bu₄NCl in H₂O with Pd(OAc)₂ catalyst. β -Aromatic carbonyl compounds are obtained in good yields. The arylation reaction is highly regioselective with respect to the addition of the aromatic group: only β -substitution is observed. The structural isomer selectivity is also very high: only traces of β -aromatic α,β -unsaturated alcohol compounds are obtained.

Catalytic Dehalogenation of Aryl Halides Mediated by a Palladium/Imidazolium Salt System

M. S. VICIU, G. A. GRASA and S. P. NOLAN, *Organometallics*, 2001, 20, (16), 3607–3612

The Pd(dba)₂/(2,4,6-trimethylphenyl)dihydroimidazolium salt system is effective for the dehalogenation of aryl chlorides, bromides, and polyhalogenated aromatic hydrocarbons. Strong bases with β -hydrogens perform both deprotonation of the imidazolium salt and are H sources for the dehalogenation process. The catalytic system does not require an excess of the ligand and appears thermally robust. The optimum metal:ligand ratio is 1:1, as 1:2 ratios give very stable and catalytically less active Pd species.

A Silica-Supported, Switchable, and Recyclable Hydroformylation–Hydrogenation Catalyst

A. J. SANDEE, J. N. H. REEK, P. C. J. KAMER and P. W. N. M. VAN LEEUWEN, *J. Am. Chem. Soc.*, 2001, 123, (35), 8468–8476

The immobilised Rh catalyst complex [Rh(A)CO]⁺ (1) (A = *N*-(3-trimethoxysilane-*n*-propyl)-4,5-bis-(diphenylphosphino)phenoxazine) was prepared via both the sol-gel process and by covalently anchoring to SiO₂. The catalyst–support interactions were fully controlled and easily manipulated by simple changes in the reaction conditions. (1) can be used both as a hydrogenation and a regioselective hydroformylation catalyst. (1) was used for a clean one-pot synthesis of 1-nonanol from 1-octene via a hydroformylation–hydrogenation cascade reaction and could be quantitatively recovered from the product.

The Activation of O₂ at Ruthenium Complexes: Catalytic Chlorination of Unsaturated Organic Substrates within the System O₂/HCl/H₂O

C. LIMBERG and J. H. TELES, *Adv. Synth. Catal.*, 2001, 343, (5), 447–449

RuCl₃ in concentrated HCl at 145°C can chlorinate aromatic compounds, such as benzene and toluene, catalytically, if O₂ is present as the oxidising agent. Similarly, bromination can be achieved in concentrated HBr. When olefins undergo chlorination, two Cl atoms are added to the double bond in an *anti* fashion, but hydrochlorination products are formed simultaneously. Halogenations proceed via electrophilic routes for the products in both types of reactions for various substrates of the 3-phase system.

Homogeneous Hydrogenation of Arenes Catalyzed by the Bis(dihydrogen) Complex [RuH₂(H₂)₂(PCy₃)₂]

A. F. BOROWSKI, S. SABO-ETIENNE and B. CHAUDRET, *J. Mol. Catal. A: Chem.*, 2001, 174, (1–2), 69–79

Cyclohexane, tetralin and a mixture of tetra- (4H-An) and octa-hydroanthracene (8H-An) were formed by reacting benzene, naphthalene and anthracene, respectively, with H₂ under 3 and 20 bar at 80°C in the presence of [RuH₂(H₂)₂(PCy₃)₂] (1). However, the increase of H₂ pressure lowers the yield of hydrogenation products. (1) may be used directly as a catalyst precursor or may be prepared *in situ* from [RuH{(η^3 -C₆H₈)PCy₂}{(η^2 -C₆H₉)PCy₂}] under H₂ at room temperature.

FUEL CELLS

Methanol Oxidation on a Carbon-Supported Pt Fuel Cell Catalyst – A Kinetic and Mechanistic Study by Differential Electrochemical Mass Spectrometry

Z. JUSYS and R. J. BEHM, *J. Phys. Chem. B*, 2001, 105, (44), 10874–10883

MeOH oxidation on a Pt/C fuel cell catalyst was investigated by online differential electrochemical mass spectrometry (DEMS) at continuous electrolyte flow and defined catalyst utilisation, using a thin film electrode setup and a thin-layer flow-through cell. MeOH-stripping DEMS experiments, oxidising the adsorbed dehydrogenation products formed on MeOH adsorption at potentials in the H adsorption region, show that its uptake depends on the electrode potential.

The Oxygen Reduction Reaction on a Pt/Carbon Fuel Cell Catalyst in the Presence of Chloride Anions

T. J. SCHMIDT, U. A. PAULUS, H. A. GASTEIGER and R. J. BEHM, *J. Electroanal. Chem.*, 2001, 508, (1–2), 41–47

For the O₂ reduction reaction (orr) on a Pt/C fuel cell catalyst, the activity was shown to decrease in the order: ClO₄⁻ > HSO₄⁻ > Cl⁻, which is consistent with the increasing adsorption bond strength of the anions. The orr properties of Pt/Vulcan in the presence of adsorbed Cl⁻ were interpreted as a superposition of the individual orr properties of the Pt(111)–Cl_{ad} and Pt(111)–Cl_{ad} solid | liquid interface.

ELECTRICAL AND ELECTRONIC ENGINEERING

Recovery Characteristics of Hydrogen-Damaged (Pb, La)(Zr, Ti)O₃ Capacitors with Pt and IrO₂ Top Electrodes

S.-G. YOON and A. I. KINGON, *J. Electrochem. Soc.*, 2001, 148, (7), F137–F139

(Pb, La)(Zr, Ti)O₃ (PLZT) film capacitors with Pt and IrO₂ top electrodes were annealed in H₂ and P-E (polarisation-field) hysteresis loops and fatigue properties were examined. The Pt/PLZT/Pt capacitor recovered fully on annealing in O₂ at 700°C, but the IrO₂/PLZT/Pt capacitor did not fully regain its ferroelectric properties. In 4% H₂ at 300°C the IrO₂ electrode was reduced to Ir. After a recovery anneal at 700°C in O₂ it changed to the IrO₂/Ir complex phase.

Influence of Combined Pt and CeO₂ Additions on Microstructure and Magnetic Properties in (Nd, Eu, Gd)–Ba–Cu–O

M. MURALIDHAR, M. JIRSA, S. NARIKI and M. MURAKAMI, *Supercond. Sci. Technol.*, 2001, 14, (10), 832–838

The effect of the combined addition of Pt and CeO₂ on the dispersion of secondary phase Gd₂BaCuO₅ (Gd-211) particles in melt-processed (Nd_{0.33}Eu_{0.33}Gd_{0.33})Ba₂Cu₃O_y (NEG-123) was studied by varying the CeO₂ content (0–3%). SEM revealed that sub- μ m-sized Gd-211 particles were distributed uniformly throughout the NEG-123 matrix for ≤ 2 mol% CeO₂. The combined addition of Pt and CeO₂ is effective in reducing the size of the secondary-phase particles.

Preparation and Properties of dc-Sputtered IrO₂ and Ir Thin Films for Oxygen Barrier Applications in Advanced Memory Technology

C. U. PINNOW, I. KASKO, C. DEHM, B. JOBST, M. SEIBT and U. GEYER, *J. Vac. Sci. Technol. B*, 2001, 19, (5), 1857–1865

Ir and IrO₂ thin films were deposited by DC sputtering in pure Ar and Ar/O₂, respectively. The stress of the Ir films can be varied from ~ -3.5 GPa for a deposition temperature of 100°C to nearly zero stress if deposited at 500°C. However, IrO₂ films exhibited a large compressive stress of ~ -1.5 GPa, which is nearly independent of substrate temperature, but changed with texture and stoichiometry of the films.

Studies of Ruthenium-Doped InP Growth by Low-Pressure Hydride Vapor-Phase Epitaxy

D. SÖDERSTRÖM, S. LOURDUDOSS, M. WALLNÄS, A. DADGAR, O. STENZEL, D. BIMBERG and H. SCHUMANN, *J. Electrochem. Soc.*, 2001, 148, (7), G375–G378

Ru-doped InP grown (1) by low-pressure hydride vapour-phase epitaxy using bis(η^5 -2,4-dimethylpentadienyl)Ru(II) produced Ru concentrations of 2×10^{15} to 2×10^{18} cm⁻³ by changing the input PH₃ and In chloride partial pressures. Resistivities for (1) of $> 10^3$ Ω cm were measured under electron injection for Ru concentration of $\geq 2 \times 10^{17}$ cm⁻³; under hole injection (1) exhibits a very high resistivity of 10^{10} Ω cm.