

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

An Original Route for the Preparation of Hard FePt

N. H. HAI, N. M. DEMPSEY, M. VERON, M. VERDIER and D. GIVORD, *J. Magn. Magn. Mater.*, 2003, 257, (2–3), L139–L145

Cyclic cold rolling was used to prepare textured Fe/Pt multilayer foils of total thickness ≈ 100 μm and individual layer thicknesses of the order of 10 nm. Ordered f.c.t. FePt ($L1_0$) was rapidly formed upon annealing at 450–550°C. Coercivities as high as 0.9 T were measured at room temperature following annealing at 450°C for 48 h. Coercivity decreased with increasing temperature: to 0.37 T at 600 K.

Adsorption and Desorption of Methanol on Pd(111) and on a Pd/V Surface Alloy

R. SCHENNACH, A. EICHLER and K. D. RENDULIC, *J. Phys. Chem. B*, 2003, 107, (11), 2552–2558

Thermal desorption spectroscopy and density functional theory established that a H bond between 2 neighbouring MeOH molecules on Pd(111) is required to break the C–O bond. This leads to formation of CH_4 . This reaction pathway is not possible on the Pd/V alloy surface, due to the different electronic structure of the alloy surface. The calculated geometries for Pd(111) and for the Pd/V alloy are very similar.

Effect of Ta Content on Martensitic Transformation Behavior of RuTa Ultrahigh Temperature Shape Memory Alloys

Z. HE, J. ZHOU and Y. FURUYA, *Mater. Sci. Eng., A*, 2003, 348, (1–2), 36–40

The martensitic transformation (MT) behaviour of $\text{Ru}_{100-x}\text{Ta}_x$ ($x = 46\text{--}54$ at.%) alloys (1) was investigated by DSC, dilatometry, XRD and optical microscopy. The one-stage reversible MT occurs in Ta-poor (1) ($\text{Ta} < 49$ at.%). The two-stage reversible MT takes place in near-equiatomic (1). No reversible MT is observed in Ta-rich (1) ($\text{Ta} > 52$ at.%). $\text{Ru}_{50}\text{Ta}_{50}$ exhibited the best MT behaviour.

CHEMICAL COMPOUNDS

Structure and Bonding of the Hexameric Platinum(II) Dichloride, $\text{Pt}_6\text{Cl}_{12}$ ($\beta\text{-PtCl}_2$)

H. G. VON SCHNERING, J.-H. CHANG, K. PETERS, E.-M. PETERS, F. R. WAGNER, Y. GRIN and G. THIELE, *Z. Anorg. Allg. Chem.*, 2003, 629, (3), 516–522

As previously reported, the structure of $\text{Pt}_6\text{Cl}_{12}$ (1) is confirmed as a hierarchical variant of the cubic structure type of W (b.c.c.), where atoms are replaced by the hexameric (1) molecules. (1) shows the (trigonally elongated) structure of the classic M_6X_{12} cluster compounds with (distorted) square-planar PtCl_4 fragments, but without metal-metal bonds.

$[\text{Pd}_{30}(\text{CO})_{26}(\text{PEt}_3)_{10}]$ and $[\text{Pd}_{54}(\text{CO})_{40}(\text{PEt}_3)_{14}]$: Generation of Nanosized Pd_{30} - and Pd_{54} -Core Geometries Containing Interpenetrating

Cuboctahedral-Based Metal Polyhedra

E. G. MEDNIKOV, S. A. IVANOV and L. F. DAHL, *Angew. Chem. Int. Ed.*, 2003, 42, (3), 323–327

$[\text{Pd}_{30}(\mu_2\text{-CO})_{22}(\mu_3\text{-CO})_4(\text{PEt}_3)_{10}]$ and $[\text{Pd}_{54}(\mu_2\text{-CO})_{32}(\mu_3\text{-CO})_8(\text{PEt}_3)_{14}]$ were synthesised as byproducts together with $[\text{Pd}_{38}(\text{CO})_{28}(\text{PEt}_3)_{12}]$ through the deligation of $[\text{Pd}_{10}(\text{CO})_{12}(\text{PEt}_3)_6]$ with CO assistance at the initial stage of the reaction. Their nanosized Pd_{30} and Pd_{54} cores are reported to be the first examples of “twinned”-core geometries involving a previously unknown oligomeric growth pattern, comprised of interpenetrating cuboctahedra as building blocks.

Palladium(II) and Palladium(0) Complexes of BINAP(O) (2-(Diphenylphosphino)-2'-(diphenylphosphinyl)-1,1'-binaphthyl)

W. J. MARSHALL and V. V. GRUSHIN, *Organometallics*, 2003, 22, (3), 555–562

The reaction of $[(\text{MeCN})_2\text{PdCl}_2]$ with BINAP(O) (1) gave $[(\text{BINAP}(\text{O}))\text{PdCl}_2]$ (2), in which (1) is P,O-chelated to Pd. Reduction of (2) with LiBH_4 , in the presence of (1) gave a new Pd(0) complex $[(\text{BINAP}(\text{O}))_2\text{Pd}]$ (3). In (3) both (1) are P-bonded to Pd and one (1) provides η^2 -arene coordination via the C=C bond adjacent to the phosphinyl group.

Rhodium(III) and Rhodium(II) Complexes of Novel Bis(oxazoline) Pincer Ligands

M. GERISCH, J. R. KRUMPER, R. G. BERGMAN and T. D. TILLEY, *Organometallics*, 2003, 22, (1), 47–58

New C_2 -symmetric bisoxazoline pincer ligands, benbox and benbox Me_2 , were used to prepare coordinately unsaturated Rh(III) complexes. Trapping reactions of $[\text{RhCl}_2\{(\text{S},\text{S})\text{-ib-benbox}(\text{Me}_2)\}]$ are described. For $[\text{RhMe}\{(\text{S},\text{S})\text{-ip-benbox}(\text{Me}_2)\}][\text{BARf}]$, Rh-to-aryl methyl migration occurs. Air-stable, mononuclear, paramagnetic Rh(II) complexes $[\text{RhCl}_2\{(\text{S},\text{S})\text{-tb-benbox}(\text{Me}_2)\}(\text{H})]$ and $[\text{RhCl}_2\{\text{dm-benbox}(\text{Me}_2)\text{H}\}]$ were isolated and characterised.

Crystal Growth of Novel Osmium-Containing Triple Perovskites

K. E. STITZER, A. EL ABED, M. D. SMITH, M. J. DAVIS, S.-J. KIM, J. DARRIET and H.-C. ZUR LOYE, *Inorg. Chem.*, 2003, 42, (4), 947–949

Single crystals of $\text{Ba}_3\text{LiOs}_2\text{O}_9$ (1) and $\text{Ba}_3\text{NaOs}_2\text{O}_9$ (2) were grown from reactive molten hydroxide fluxes in sealed Ag tubes. (1) and (2) crystallise in the space group $\text{P6}_3/\text{mmc}$ with lattice parameters of $a = 5.8025(1)$ \AA , $c = 14.1468(4)$ \AA for (1) and $a = 5.8858(1)$ \AA , $c = 14.3451(5)$ \AA for (2).

ELECTROCHEMISTRY

Ruthenium Based DSA® in Chlorate Electrolysis—Critical Anode Potential and Reaction Kinetics

A. CORNELL, B. HÅKANSSON and G. LINDBERGH, *Electrochim. Acta*, 2003, 48, (5), 473–481

Ru-based DSA®s were investigated in chlorate electrolyte using rotating discs made from commercial electrodes. The voltammetric charge and iR -corrected polarisation curves, up to current densities of 40 kA m⁻², were recorded on new anodes and on aged anodes after 3 years in use. New anodes for chlorate electrolysis that work at a potential > critical potential, E_{CR} , will develop an increase in real surface area during the first months of operation.

PHOTOCONVERSION

Room Temperature Phosphorescence from a Platinum(II) Diimine Bis(pyrenylacetyl)ide Complex

I. E. POMESTCHENKO, C. R. LUMAN, M. HISSLER, R. ZIESSEL and F. N. CASTELLANO, *Inorg. Chem.*, 2003, 42, (5), 1394–1396

Long-lived, room temperature phosphorescence was observed in Pt(dbbpy)(C≡C-pyrene)₂ (dbbpy = 4,4'-di(*tert*-butyl)-2,2'-bipyridine; C≡C-pyrene = 1-ethynylpyrene) in fluid solution. The static and time-resolved absorption and luminescence data are consistent with phosphorescence emerging from the C≡C-pyrenyl units following excitation into the low energy MLCT absorption bands.

Laser Photolysis Studies of Rhodium(III) Porphyrins. Photodissociation of Axial Phosphine Ligand in the Temperature Range 300–200 K

H. SUZUKI, Y. MIYAZAKI and M. HOSHINO, *J. Phys. Chem. A*, 2003, 107, (9), 1239–1245

The photodissociation of the axial PPh₃ ligand of (X⁻)(PPh₃)Rh^{III}OEP (1) and (X⁻)(PPh₃)Rh^{III}TPP (2) (X = Cl, Br, I) in toluene was studied by 355 nm laser flash photolysis. The photodissociation yield of PPh₃, Φ , from (1) is dependent on the nature of X: $\Phi = 0.79$ for X = I, $\Phi = 0.48$ for X = Br and $\Phi = 0$ for X = Cl. Similar trends are observed for (2): $\Phi = 0.13$ for X = I and $\Phi = 0$ for X = Br, Cl.

Extending the Luminescence Lifetime of Ruthenium(II) Poly(pyridine) Complexes in Solution at Ambient Temperature

A. HARRIMAN, A. KHATYR and R. ZIESSEL, *Dalton Trans.*, 2003, (10), 2061–2068

Synthesised Ru(II) poly(pyridine)s have a central diethynylated pyrene moiety separating the 2,2'-bipy and 2,2':6',2''-terpyridine-based terminals. The mononuclear complex, having only bipy coordinated with the metal cation, and the corresponding binuclear complex show remarkably similar luminescence properties in deoxygenated MeCN at room temperature. Two emission bands are present in the spectrum. The phosphorescence lifetimes are significantly longer than those of the parent complexes. At low temperature, only the MLCT triplet is observed.

ELECTRODEPOSITION AND SURFACE COATINGS

Nucleation and Growth of Electroless Palladium Deposition on Polycrystalline TiN Barrier Films for Electroless Copper Deposition

S. W. HONG, Y. S. LEE, K.-C. PARK and J.-W. PARK, *J. Electrochem. Soc.*, 2003, 150, (1), C16–C18

The nucleation and growth of electrochemically deposited Pd on DC magnetron sputtered polycrystalline TiN thin films (1) were investigated. The growth of the Pd nuclei on (1) was 3D island growth. Plan-view TEM images of electrochemically nucleated Pd on (1) for 5 s showed that the Pd nuclei were mainly formed on the grain boundaries of (1), especially on the grain boundary triple points.

Iridium Coatings Grown by Metal–Organic Chemical Vapor Deposition in a Hot-Wall CVD Reactor

F. MAURY and F. SENOCQ, *Surf. Coat. Technol.*, 2003, 163–164, 208–213

Ir thin films (1) were deposited on W substrates by thermal decomposition of Ir(COD)(MeCp) in H₂ or O₂. The growth was carried out in a horizontal hot-wall MOCVD reactor under reduced pressure at 573–673 K. The process is more difficult to control using H₂. O₂ avoids C incorporation in layers of (1) and significantly enhances the growth rate. However, codeposition of Ir and IrO₂ was observed on using a high O₂ excess. (1) with uniform thickness (1–2 μm) over a length of ~ 15 cm were achievable.

Ruthenium Thin Films Grown by Atomic Layer Deposition

T. AALTONEN, P. ALÉN, M. RITALA and M. LESKELÄ, *Chem. Vap. Deposition*, 2003, 9, (1), 45–49

High quality Ru films (1) were grown by atomic layer deposition at 275–400°C using RuCp₂ and O₂ precursors. (1) were deposited on thin Al₂O₃ and TiO₂ films on glass. XRD analysis indicated that (1) were polycrystalline metallic Ru and SEM showed that (1) had excellent conformality. (1) grown at 350°C contained < 0.2 at.% C, < 0.2 at.% H and < 0.4 at.% O, and had resistivity of 13 μΩ cm.

APPARATUS AND TECHNIQUE

On the Platinum Sensitization of Nanosized Cerium Dioxide Oxygen Sensors

S. V. MANORAMA, N. IZU, W. SHIN, I. MATSUBARA and N. MURAYAMA, *Sens. Actuators B, Chem.*, 2003, 89, (3), 299–304

O sensors using nanosized CeO₂ had improved sensitivity and response time, t_{90} , compared with those using coarse-grained CeO₂. Pt incorporated into CeO₂ also increased the sensitivity and decreased t_{90} at 1081–1178 K, the optimum operating temperature. This is due to its catalytic role and its presence making O vacancy formation favourable.

Preparation of Thin and Highly Stable Pd/Ag Composite Membranes and Simulative Analysis of Transfer Resistance for Hydrogen Separation

K. HOU and R. HUGHES, *J. Membrane Sci.*, 2003, 214, (1), 43–55

Composite Pd/Ag membranes on an α -Al₂O₃ substrate were prepared by sequential electroless plating. SEM showed that the Pd/Ag film was of columnar form perpendicular to the substrate. Annealing the separate Pd and Ag deposited layers at > 600°C in H₂ gave homogeneous Pd/Ag alloy films. H₂ fluxes \leq 0.35 mol m⁻² s⁻¹ and H₂/N₂ selectivities of 4500 were obtained. Long term thermal cycling tests at two pressures showed that the membranes are stable.

High-Performance Taste Sensor Made from Langmuir–Blodgett Films of Conducting Polymers and a Ruthenium Complex

M. FERREIRA, A. RIUL, K. WOHNATH, F. J. FONSECA, O. N. OLIVEIRA and L. H. C. MATTOSO, *Anal. Chem.*, 2003, 75, (4), 953–955

A sensor array consisting of nanostructured LB films can be used as an electronic tongue capable of identifying sucrose, quinine, NaCl and HCl at the ppb level. The sensing units comprise LB films from conducting polymers and *mer*-[RuCl₃(dppb)(py)] (dppb = PPh₂(CH₂)₄PPh₂; py = pyridine) transferred onto Au interdigitated electrodes. Impedance spectroscopy is used in the detection.

HETEROGENEOUS CATALYSIS

Study of Structure-Function Relationships in Platinum-Silica Catalysts Using Hydrocarbon Hydrogenation as a Probe Reaction

E. DIAS, A. T. DAVIES, M. D. MANTLE, D. ROY and L. F. GLADDEN, *Chem. Eng. Sci.*, 2003, 58, (3–6), 621–626

Solid-state NMR and Raman spectroscopy were used to characterise Si environments in the structure of 0.5 wt.% Pt/SiO₂ (1), in particular strained siloxane ring environments. Reactor data are reported for ethene and ethyne hydrogenation reactions with (1) as catalysts. The results indicate that catalytic activity is determined by metal surface area, which is controlled by the method of metal deposition. The selectivity of ethyne hydrogenation to ethane appears to correlate with the structure of the SiO₂ surface.

Solventless Suzuki Coupling Reactions on Palladium-Doped Potassium Fluoride Alumina

G. W. KABALKA, L. WANG, R. M. PAGNI, C. M. HAIR and V. NAMBOODIRI, *Synthesis*, 2003, (2), 217–222

Solventless Suzuki couplings have been achieved using KF/Al₂O₃ mixtures and Pd powder. Aryl iodides react faster than the bromides or chlorides; aryl groups are also more reactive than alkenyl groups, which react faster than alkyl groups. The use of microwave irradiation reduces reaction times from hours to minutes. The Pd catalyst can be recycled using a simple filtration and washing sequence.

Direct Synthesis of Propylene Oxide with CO₂ as the Solvent

T. DANCIU, E. J. BECKMAN, D. HANCU, R. N. COCHRAN, R. GREY, D. M. HAJNIK and J. JEWSON, *Angew. Chem. Int. Ed.*, 2003, 42, (10), 1140–1142

CO₂ was used as the sole solvent for the clean one-step generation of propylene oxide (PO) from H₂, O₂ and propylene over the catalyst Pd/Ti silicalite (TS-1). CO₂ can solubilise large quantities of gases, is miscible with both propylene and PO, and is chemically inert to the PO product. Therefore MeOH is not required for the efficient production of PO from propylene and H₂O₂ produced *in situ* as was previously suggested.

Reductions of Aromatic Amino Acids and Derivatives

D. J. AGER and I. PRAKASH, *Org. Process Res. Dev.*, 2003, 7, (2), 164–167

The reduction of aromatic amino acid derivatives to the corresponding cyclohexyl compounds without racemisation of the amino acids was achieved with H₂ at low pressure over Rh/Al₂O₃ or Rh/C catalyst. The Rh/C catalyst was only effective under acidic conditions (HCl, H₂SO₄, H₃PO₄). The procedure can be scaled up to prepare multikilogram quantities of the products.

Highly Efficient Liquid-Phase Oxidation of Primary Alcohols to Aldehydes with Oxygen Catalysed by Ru–Co Oxide

M. MUSAWIR, P. N. DAVEY, G. KELLY and I. V. KOZHEVNIKOV, *Chem. Commun.*, 2003, (12), 1414–1415

Ru^{IV}-Co^{III} (1:1.5) binary oxide (1), prepared by coprecipitation, was found to be a highly efficient catalyst for the oxidation of primary alcohols to aldehydes (76–95% selectivity at 54–100% conversion) with O₂ or air. The oxidation was carried out under atmospheric pressure at 80–110°C in solvents such as toluene, acetonitrile or dichloroethane; toluene being the best solvent. (1) was reusable, but with gradually declining activity. The Co may have a significant role in the activation of O₂ in catalyst reoxidation.

HOMOGENEOUS CATALYSIS

Dispersing Palladium Nanoparticles Using a Water-in-Oil Microemulsion–Homogenization of Heterogeneous Catalysis

B. YOON, H. KIM and C. M. WAI, *Chem. Commun.*, 2003, (9), 1040–1041

Pd nanoparticles (1) were dispersed in a H₂O/AOT/*n*-hexane microemulsion by H₂ gas reduction of PdCl₂. TEM showed the presence of spherical Pd metallic particles with diameters of 4–10 nm. (1) are very efficient catalysts for hydrogenation of olefins such as 1-phenyl-1-cyclohexene, methyl *trans*-cinnamate and *trans*-stilbene in *n*-hexane. (1) are stable for ~ 15–20 minutes. (1) could be separated from the *n*-hexane solution by filtration.

A Novel Methodology for Efficient Removal of Residual Palladium from a Product of the Suzuki–Miyaura Coupling with Polymer-Supported Ethylenediamine Derivatives

Y. URAWA, M. MIYAZAWA, N. OZEKI and K. OGURA, *Org. Process Res. Dev.*, 2003, 7, (2), 191–195

Polymer-bound ethylenediamines (1) were used to remove residual Pd from the crude 2'-cyanobiphenyl product obtained by the Suzuki–Miyaura coupling of an optically active bromobenzene derivative with a boronate using PdCl₂(PPh₃)₂ catalyst. Treatment with (1) reduced the Pd content of the crude product from 2000–3000 to 100–300 ppm. Subsequent purification by salt formation with di-*p*-toluoyl-D-tartaric acid gave a low Pd content of < 10 ppm.

Development of a 9-Borabicyclo[3.3.1]nonane-Mediated Solid-Phase Suzuki Coupling for the Preparation of Dihydrostilbene Analogs

R. D. FERGUSON, N. SU and R. A. SMITH, *Tetrahedron Lett.*, 2003, 44, (14), 2939–2942

A novel 9-borabicyclo[3.3.1]nonane (9-BBN)-mediated solid-phase Suzuki coupling was used to prepare dihydrostilbenes and related derivatives. Under optimised conditions (20 mol% PdCl₂(dppf), 10 equiv. Et₃N and 10 equiv. olefin/9-BBN in DMF/H₂O (9:1) at 50°C for 18 h) high conversions were achieved. This methodology was applied to the preparation of a combinatorial library.

New *P,N*-Ferrocenyl Ligands for Rhodium-Catalyzed Hydroboration and Palladium-Catalyzed Allylic Alkylation

R. J. KLOETZING, M. LOTZ and P. KNOCHEL, *Tetrahedron: Asymmetry*, 2003, 14, (2), 255–264

Nine new chiral *P,N*-ferrocenyl ligands (1) were prepared and used in metal-catalysed enantioselective reactions. The Pd-catalysed asymmetric alkylation of 1,3-diphenylallylic systems (≤ 94% ee) gave good results. The Rh-catalysed hydroboration of styrene with catechol borane proceeded with high regioselectivity (≤ 97:3) or with high enantioselectivity (≤ 92% ee) depending on the catalyst. Fine tuning of (1) had a significant influence on the performance.

Synthesis of a Conjugated Star Polymer and Star Block Copolymers Based on the Living Polymerization of Phenylacetylenes with a Rh Catalyst

K. KANKI and T. MASUDA, *Macromolecules*, 2003, 36, (5), 1500–1504

1,4-Diethynylbenzene was used as linking agent in the living polymerisation system of phenylacetylene by [(nbd)RhCl]₂/Ph₂C=C(Ph)Li/Ph₃P (nbd = norbornadiene). The *M_n* and arm number of a typical star polymer formed by this system were 145,000 and 25, respectively. The arm number of the star polymer increased with increasing concentration of the linking agent, temperature of the linking reaction and with decreasing DP_n of the linear polymer.

Hydroformylation Studies Using Nafion Supported Rhodium Based Homogeneous Catalysts

D. E. BRYANT and M. KILNER, *J. Mol. Catal. A: Chem.*, 2003, 193, (1–2), 83–88

[Rh(L)₂NBD]BF₄ (1) and [Rh(L-L)NBD]BF₄ (2) (L = a phosphine ligand; L-L = a diphosphine ligand; NBD = norbornadiene) were prepared. (1) and (2) were incorporated into Nafion by ion exchange. These supported catalysts were compared with their homogeneous precursors for their activity as catalysts for hex-1-ene hydroformylation. The overall yield and ratio of normal heptanal to branched products are reduced in all cases by the supported catalysts.

Transition-Metal Nanocluster Catalysts: Scaled-up Synthesis, Characterization, Storage Conditions, Stability, and Catalytic Activity before and after Storage of Polyoxoanion- and Tetrabutylammonium-Stabilized Ir(0) Nanoclusters

B. J. HORNSTEIN and R. G. FINKE, *Chem. Mater.*, 2003, 15, (4), 899–909

Isolated, 3.8 ± 0.6 nm Ir(0)_{~2000} nanoclusters (1) (~ 1 g), stabilised by P₂W₁₅Nb₃O₆₂⁹⁻ and (*n*-C₄H₉)₄N⁺, in propylene carbonate solvent, have been synthesised. (1) retain ~ 65% of their as-formed catalytic activity for cyclohexene hydrogenation. (1) maintain their activity to within ± 15% for 6 weeks when stored as a solid under N₂ in a ≤ 5 ppm O₂ drybox. (1) are more stable when stored under 40 psig H₂.

Dimethyl Carbonate–Water: an Environmentally Friendly Solvent System for Ruthenium Tetraoxide Oxidations

J. CORNELLY, L. M. SU HAM, D. E. MEADE and V. DRAGOJLOVIC, *Green Chem.*, 2003, 5, (1), 34–37

Dimethyl carbonate–H₂O was used as solvent in RuO₄ oxidations of alkenes, alkynes, arenes, alcohols, ethers and aldehydes. Either hydrated RuCl₃ or hydrated RuO₂ was used as the source of Ru. Suitable cooxidants include Na periodate, bleach and Oxone®. RuO₄, with bleach as cooxidant, may find use in the oxidative degradation of organic pollutants.

FUEL CELLS

High Performance Carbon-Supported Catalysts for Fuel Cells via Phosphonation

Z. XU, Z. QI and A. KAUFMAN, *Chem. Commun.*, 2003, (7), 878–879

Pt/C was phosphonated using 2-aminoethylphosphonic acid to give Pt/carbon-CH₂CH₂PO₃H₂ catalysts (1). (1) have largely enhanced proton conductivity and performed substantially better than the untreated counterparts in PEMFCs. Even with 10% less Nafion, the phosphonated catalyst has 20% higher performance over the entire current density region. The highest power densities achieved by phosphonated and unphosphonated catalysts were 0.57 and 0.47 W cm⁻², respectively.

Methanol Electrochemistry at Carbon-Supported Pt and PtRu Fuel Cell Catalysts: Voltammetric and in Situ Infrared Spectroscopic Measurements at 23 and 60°C

G. VIJAYARAGHAVAN, L. GAO and C. KORZENIEWSKI, *Langmuir*, 2003, 19, (6), 2333–2337

The electrochemical oxidation of MeOH (50–200 mM) in 0.1 M HClO₄ on thin films of Pt (10 wt.%) (1) and PtRu (30 wt.% Pt, 15 wt.% Ru) (2) supported on Vulcan XC-72R C on bulk Au was investigated. MeOH electrooxidation was more sluggish on (1) than on either bulk polycrystalline Pt or (2). (2) was more resistant than bulk PtRu to CO adsorption.

Preparation of Methanol Oxidation

Electrocatalysts: Ruthenium Deposition on Carbon-Supported Platinum Nanoparticles

F. MAILLARD, F. GLOAGUEN and J.-M. LEGER, *J. Appl. Electrochem.*, 2003, 33, (1), 1–8

MeOH oxidation electrocatalysts were prepared by Ru electrochemical or spontaneous deposition on Pt nanoparticles/Vulcan XC72 C. The maximum electrocatalytic activity for MeOH oxidation at room temperature was observed at lower Ru coverage ($\theta_{Ru} \sim 10\%$) for spontaneous deposition than for electrodeposition ($\theta_{Ru} \sim 20\%$). However, higher current densities for MeOH oxidation were obtained with electrodeposited Ru.

Electrocatalytic Enhancement of Methanol Oxidation at Pt-WO_x Nanophase Electrodes and In-Situ Observation of Hydrogen Spillover Using Electrochromism

K.-W. PARK, K.-S. AHN, Y.-C. NAH, J.-H. CHOI and Y.-E. SUNG, *J. Phys. Chem. B*, 2003, 107, (18), 4352–4355

Pt-WO_x and WO_x thin film electrodes were grown using RF magnetron cosputtering. The Pt-WO_x nanophase electrode had enhanced electrocatalytic activity compared to Pt itself for MeOH oxidation and exactly the reverse change in optical signal intensity with respect to electrochemical cell potential, compared with an electrochromic WO_x electrode.

ELECTRICAL AND ELECTRONIC ENGINEERING

Microstructural Study of Pt Contact on p-Type GaN

J. K. KIM, H. W. JANG, C. C. KIM, J. H. JE, K. A. RICKERT, T. F. KUECH and J.-L. LEE, *J. Vac. Sci. Technol. B*, 2003, 21, (1), 87–90

A Pt layer was shown to grow epitaxially on GaN. Due to a lattice mismatch between Pt and GaN, a biaxial tensile strain (+0.9%) to the Pt layer and a compressive strain (–0.9%) to the GaN substrate were introduced in the as-deposited state. After annealing at 450°C, the strains became fully relaxed and the position of the surface Fermi level moved 0.21 eV toward the valence band maximum. The contact resistivity decreased by 1 order of magnitude.

MEDICAL USES

The First Examples of Platinum Amine Hydroxamate Complexes: Structures and Biological Activity

T. W. FAILLES, M. D. HALL and T. W. HAMBLEY, *Dalton Trans.*, 2003, (8), 1596–1600

$\{[Pt(en)_2(\mu-bha)]ClO_4 \cdot H_2O\}$ and $\{[Pt(R,R-chxn)_2(\mu-bha)]NO_3 \cdot 2H_2O\}$ have two Pt centres that are bridged through the bha ligand *via* (O,O) and (C,N) coordination modes, the latter mode occurring through deprotonation of the *ortho* C of the phenyl ring. The cytotoxicities of these dinuclear complexes were tested. Both complexes were less active than their corresponding dichloro parent complexes.

Synthesis and Antitumour Activity of DNA Binding Cationic Porphyrin-Platinum(II) Complexes

R. SONG, Y.-S. KIM, C. O. LEE and Y. S. SOHN, *Tetrahedron Lett.*, 2003, 44, (8), 1537–1540

DNA binding 5,10,15-tris(*N*-methyl-4-pyridiniumyl)porphyrin (TrisMPyP)-Pt(II) conjugates (1) were synthesised, in which different spacer ligands were used for appropriate coordination to Pt(II) complexes. (1) exhibited high antitumour activity superior to cisplatin and an elevated tumour-localising effect (tumour:muscle ratio > 2) compared to carboplatin.

Synthesis and Characterisation of Some Water Soluble Ruthenium(II)-Arene Complexes and an Investigation of Their Antibiotic and Antiviral Properties

C. S. ALLARDYCE, P. J. DYSON, D. J. ELLIS, P. A. SALTER and R. SCOPELLITI, *J. Organomet. Chem.*, 2003, 668, (1–2), 35–42

Complexes $[Ru(\eta^6-p-cymene)X_2]_2$ (X = Cl, Br, I, NCS), $[Ru(\eta^6-p-cymene)X_2(pta)]$ (pta = 1,3,5-triaza-7-phosphatricyclo[3.3.1.1]decane) and the tetra-ruthenium cluster $[H_4Ru_4(\eta^6-p-benzene)_4]^{2+}$ (1) were prepared and their antimicrobial properties evaluated. The antimicrobial activity of these complexes may be due to their specific interactions with proteins, but appears not to be correlated with DNA binding. (1) inhibited the growth of the Polio virus but did not affect the growth of human cells.

Ruthenium(III) Polyaminocarboxylate Complexes: Efficient and Effective Nitric Oxide Scavengers

B. R. CAMERON, M. C. DARKES, H. YEE, M. OLSEN, S. P. FRICKER, R. T. SKERLJ, G. J. BRIDGER, N. A. DAVIES, M. T. WILSON, D. J. ROSE and J. ZUBIETA, *Inorg. Chem.*, 2003, 42, (6), 1868–1876

Two Ru^{III} polyaminocarboxylate complexes, AMD6245 (1) and AMD6221 (2), and their nitrosyl analogues, AMD6204, AMD6263 and AMD3689, were prepared and characterised. Upon reaction with NO, (1) and (2) formed a linear, diamagnetic $\{RuNO\}^6$ complex. (1) and (2) have an impact on the amount of nitrite accumulation in cell media in the RAW264 murine macrophage assay (an estimation of the NO scavenging ability).