

ABSTRACTS

of current literature on the platinum metals and their alloys

CHEMICAL COMPOUNDS

Dimeric Palladium Complexes with Bridging Aryl Groups: When Are They Stable?

A. C. ALBÉNIZ, P. ESPINET, O. LÓPEZ-CIMAS and B. MARTÍN-RUIZ, *Chem. Eur. J.*, 2005, 11, (1), 242–252

$[\text{Pd}_2(\mu\text{-R})_2(\eta^3\text{-allyl})_2]$ (R = haloaryl, mesityl) were prepared. The haloaryl complexes exchange between their *cis* and *trans* isomers (relative to the orientation of the two allyl groups in the dimer) by solvent-assisted associative bridge splitting. Stable aryl bridges are favoured by ancillary ligands of small size and lacking electron lone pairs, and aryl ligands reluctant to be involved in homo and hetero C–C coupling.

Synthesis, Structure and Electrochemical Properties of Tris-picolinate Complexes of Rhodium and Iridium

S. BASU, S.-M. PENG, G.-H. LEE and S. BHATTACHARYA, *Polyhedron*, 2005, 24, (1), 157–163

The pic ligands of $[\text{M}(\text{pic})_3]$ (M = Rh, Ir; Hpic = picolinic acid) are coordinated as bidentate N₂O-donors. A water of crystallisation molecule is H bonded to the carboxylate fragments of two adjacent (1) and acts a bridge between the individual (1). (1) are diamagnetic and show intense MLCT transitions in the visible region. CV on (1) shows a M(III)–M(IV) oxidation and a ligand-centred reductive response.

Iridium(I) and Rhodium(I) Cationic Complexes with Triphosphinocalix[6]arene Ligands: Dynamic Motion with Size-Selective Molecular Encapsulation

Y. OBORA, Y. K. LIU, L. H. JIANG, K. TAKENAKA, M. TOKUNAGA and Y. TSUJI, *Organometallics*, 2005, 24, (1), 4–6

The title complexes (1) exhibited dynamic behaviour with size-selective molecular encapsulation. Variable-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR measurements were carried out in the presence of various molecules (1). (1) were divided into three groups, depending on the maximum projection area of the solvent-accessible surface, A : < 45 Å², 45–68 Å², and > 68 Å². Molecules with A of 45–68 Å² just fit in the cavity and slow the dynamic behaviour.

Synthesis and Derivatization of Iridium(I) and Iridium(III) Pentamethyl[60]fullerene Complexes

Y. MATSUO, A. IWASHITA and E. NAKAMURA, *Organometallics*, 2005, 24, (1), 89–95

$\text{Ir}(\eta^5\text{-C}_{60}\text{Me}_5)(\text{CO})_2$ (1) was obtained from the reaction of $\text{K}(\text{C}_{60}\text{Me}_5)$ with $[\text{IrCl}(\text{CO})_2]_2$ in MeCN/THF. Oxidation of the Ir atom of (1) by I_2 gave an Ir(III) complex, $\text{Ir}(\eta^5\text{-C}_{60}\text{Me}_5)_2(\text{CO})$ (2). The iodo and carbonyl ligands of (2) can be readily replaced by alkyl, alkynyl, phosphine, and isonitrile ligands. (2) may be used as catalysts for organic synthesis.

ELECTROCHEMISTRY

Electrochemical Investigations of Platinum Phenylethyne Complexes

L. KONDRACHOVA, K. E. PARIS, P. C. SANCHEZ, A. M. VEGA, R. PYATI and C. D. RITHNER, *J. Electroanal. Chem.*, 2005, 576, (2), 287–294

Pt phenylethyne complexes exhibited irreversible oxidations in benzene/MeCN near +1.2 V vs. Ag|AgCl. However, *trans*-bis(tri-*n*-butylphosphine) bis(phenylethyne)platinum(II) underwent reduction in THF at –2.786 V. Photophysical measurements established that as the phenylethyne chain length increases, the absorbance wavelength increases. The emission wavelength shows a weak but similar trend.

Controlled Growth of a Single Palladium Nanowire between Microfabricated Electrodes

M. A. BANGAR, K. RAMANATHAN, M. YUN, C. LEE, C. HANGARTER and N. V. MYUNG, *Chem. Mater.*, 2004, 16, (24), 4955–4959

Dimensionally controlled growth of a single Pd nanowire (1) between pre-microfabricated Au electrodes was achieved using an electrochemical method. (1) of 100 nm, 500 nm, and 1 μm wide and 2.5 μm long channels (length-to-diameter ratio ~ 2.5–25) were grown. Current of –100 nA was used.

PHOTOCONVERSION

A Luminescent Pt(II) Complex with a Terpyridine-Like Ligand Involving a Six-Membered Chelate Ring

Y.-Z. HU, M. H. WILSON, R. ZONG, C. BONNEFOUS, D. R. McMILLIN and R. P. THUMMEL, *Dalton Trans.*, 2005, (2), 354–358

$[\text{Pt}(\text{1})\text{Cl}]^+$ (2) ((1) = 2-(8'-quinolinyl)-1,10-phenanthroline) was prepared. The six-membered chelate ring in (2) gives relief to the angle strain as well as some non-planarity in bound (1). In CH_2Cl_2 (2) exhibited higher energy charge-transfer absorption, but slightly lower energy emission than $[\text{Pt}(\text{3})\text{Cl}]^+$ ((3) = 2-(2'-pyridyl)-1,10-phenanthroline).

Electrochemical and Luminescent Properties of New Mononuclear Ruthenium(II) and Binuclear Iridium(III)–Ruthenium(II) Terpyridine Complexes

N. YOSHIKAWA, T. MATSUMURA-INOUE, N. KANEHISA, Y. KAI, H. TAKASHIMA and K. TSUKAHARA, *Anal. Sci.*, 2004, 20, (12), 1639–1644

The title complexes include $[\text{Ru}^{\text{II}}_2\text{Cl}_2(\text{dpp})(\text{terpy})_2]^{2+}$ (1) and $[\text{Ir}^{\text{III}}\text{Ru}^{\text{II}}\text{Cl}_2(\text{dpp})(\text{terpy})_2]^{3+}$ (2) (dpp = 2,3-bis(2-pyridyl)pyrazine). The absorption spectra of (1) and (2) exhibit ligand-centred bands in the UV region and MLCT bands in the visible region. The HOMO is based on Ru, and the LUMO is dpp-based.

Design of Novel Efficient Sensitizing Dye for Nanocrystalline TiO₂ Solar Cell; Tripyridine-thiolato (4,4',4''-tricarboxy-2,2':6',2''-terpyridine) ruthenium(II)

F. AIGA and T. TADA, *Sol. Energy Mater. Sol. Cells*, 2005, 85, (3), 437–446

The title Ru complex (1) was designed based on the DFT MO calculations with PBE0 functional. (1) is a modification of the Ru black dye (2), with the NCS ligands of (2) being replaced by C₅H₄NS ligands. (1) has a higher electron transfer rate from redox systems to oxidised dyes and higher absorption efficiency to the solar spectrum.

A Highly Efficient Redox Chromophore for Simultaneous Application in a Photoelectrochemical Dye Sensitized Solar Cell and Electrochromic Devices

A. F. NOGUEIRA, S. H. TOMA, M. VIDOTTI, A. L. B. FORMIGA, S. I. CORDOBA DE TORRESI and H. E. TOMA, *New J. Chem.*, 2005, 29, (2), 320–324

Na₆[{Ru^{II}(dicarboxybipyridine)₂Cl₂(BPEB)}] (1) (BPEB = *trans*-1,4-bis[2-(4-pyridyl)ethenyl]benzene) exhibits an electrochromic effect when reduced. The carboxylate groups of the bipyridine allow strong attachment to the surface of TiO₂. This contributes to an efficient and reversible electron transfer from the oxide to the chromophoric ligand, colouring the oxide film blue. (1) also has a high photon-to-electron conversion efficiency when applied as a photoanode in a dye sensitised solar cell.

ELECTRODEPOSITION AND SURFACE COATINGS

Characterizations of Pd–Ag Membrane Prepared by Sequential Electroless Deposition

W.-H. LIN and H.-F. CHANG, *Surf. Coat. Technol.*, 2005, 194, (1), 157–166

Sequential electroless plating on porous stainless steel was used to prepare Pd–Ag membranes. AFM established that lower skin layer roughness and lower deposition rate were related. EDS confirmed the Pd–Ag deposit over and inside of the porous substrate to be homogeneous.

Preparation of Palladium and Silver Alloy Membrane on a Porous α -Alumina Tube via a Simultaneous Electroless Plating

D. A. PACHECO TANAKA, M. A. LLOSA TANCO, S. NIWA, Y. WAKUI, F. MIZUKAMI, T. NAMBA and T. M. SUZUKI, *J. Membrane Sci.*, 2005, 247, (1–2), 21–27

For the title process, seeding of Pd nanoparticles (1) on an α -Al₂O₃ tube allowed codeposition of Pd and Ag. (1) were distributed by dip-coating with Pd acetate or [Pd(acac)₂] in organic solvents followed by reduction with alkaline hydrazine solution. After simultaneous deposition, alloying of Pd and Ag was carried out at 500°C for 4 h in H₂.

Morphological Evolution of the Self-Assembled IrO₂ One-Dimensional Nanocrystals

R.-S. CHEN, H.-M. CHANG, Y.-S. HUANG, D.-S. TSAI and K.-C. CHIU, *Nanotechnology*, 2005, 16, (1), 93–97

The morphological evolution of IrO₂ 1D nanocrystals (1) via MOCVD has been observed. (1) result from a decrease in the degree of interface instability. (1) occur from triangular/wedged nanorods via incomplete/scrolled nanotubes to square nanotubes and square nanorods. The polycrystalline films composed of continuous 3D grains belong to the most stable form as compared to the 1D nanocrystals.

Thermophysical Properties and Deposition of B2 Structure Based Al–Ni–Ru–M Alloys

I. VJUNITSKY, P. P. BANDYOPADHYAY, St. SIEGMANN, M. DVORAK, E. SCHÖNFELD, T. KAISER, W. STEURER and V. SHKLOVER, *Surf. Coat. Technol.*, 2005, 192, (2–3), 131–138

The normal value range for the thermal conductivity of the title alloys is 10–20 W m⁻¹ K⁻¹ at room temperature, but can be reduced to ~ 3.5 W m⁻¹ K⁻¹ by modifying the alloy composition. A fused and subsequently pulverised Al–Ni–Ru alloy was deposited on a Ni-based superalloy (modified CMSX-4) using vacuum and atmospheric plasma spraying. The coatings had favourable coating–substrate adhesion. A segregated intermetallic phase was detected at the Al₅₀Ni₄₀Ru₁₀/modified CMSX-4 interface.

APPARATUS AND TECHNIQUE

Fabrication and Characterisation of Ultra-Thin Tungsten–Carbon (W/C) and Platinum–Carbon (Pt/C) Multilayers for X-Ray Mirrors

B. K. GAN, B. A. LAPELLA and R. W. CHEARY, *Appl. Surf. Sci.*, 2005, 239, (2), 237–245

Ultra-thin Pt/C and W/C multilayer films (1) were fabricated using DC magnetron sputtering. The bilayer period and the total number of layers were varied to ascertain the X-ray reflectance response. XPS established that a distinct intermixing layer develops in (1). (1) are mechanically reliable and have excellent adhesion. Hardness and Young's modulus improved with increasing number of layers. (1) have potential as mirrors for high energy X-ray applications.

Morphological Study of Supported Thin Pd and Pd–25Ag Membranes upon Hydrogen Permeation

Y. ZHANG, M. KOMAKI and C. NISHIMURA, *J. Membrane Sci.*, 2005, 246, (2), 173–180

H₂ permeation of Pd and Pd–25Ag membranes supported by V–15Ni was investigated at 423–673 K. The Pd–25Ag membrane was more resistant to H-induced cracking and grain growth. H permeation of the Pd–25Ag/V–15Ni membrane (1) was carried out at 573 and 673 K for 200 h. At 573 K, small amounts of oxide formed on the Pd–Ag surface. Whisker and fissure-oxide morphologies were dominant on the exit and entrance side of (1), respectively, along with severe metallic interdiffusion, at 673 K.

HETEROGENEOUS CATALYSIS

Preparation and Characterisation of Pt Containing NbMCM-41 Mesoporous Molecular Sieves Addressed to Catalytic NO Reduction by Hydrocarbons

I. SOBCZAK, M. ZIOLEK and M. NOWACKA, *Microporous Mesoporous Mater.*, 2005, 78, (2–3), 103–116

The title catalysts were prepared via impregnation of NbMCM-41 with $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ or H_2PtCl_6 (1 wt.% of Pt). Smaller size Pt clusters were obtained with H_2PtCl_6 . A FTIR study with $\text{NO} + \text{O}_2 + \text{C}_3\text{H}_6$ indicated that Pt/NbMCM-41 has potential for the SCR process. The NbO^+ species enhance the oxidative activity in $\text{NO} \rightarrow \text{NO}_2$, whereas the Pt species is responsible for hydrocarbon activation. NbMCM-41 acts as storage for the nitrate/nitrite species.

Flame-Made Pd/La₂O₃/Al₂O₃ Nanoparticles: Thermal Stability and Catalytic Behavior in Methane Combustion

R. STROBEL, S. E. PRATSINIS and A. BAIKER, *J. Mater. Chem.*, 2005, 15, (5), 605–610

Flame spray pyrolysis was used to prepare Pd nanoparticles (< 5 nm) supported on La-stabilised Al_2O_3 (1) with specific surface areas of 50–180 $\text{m}^2 \text{g}^{-1}$. (1) was tested for the catalytic combustion of CH_4 . (1) exhibited excellent thermal stability in terms of specific surface area up to 1200°C and retarded γ - to α - Al_2O_3 transformation. (1) was tested as-prepared and after sintering at 1000°C (Pd particles, 50–150 nm). All the materials exhibited similar catalytic performance after an initial conditioning cycle if the temperature was cycled several times (200–1000°C).

Effect of the Promoter and Support on the Catalytic Activity of Pd–CeO₂-Supported Catalysts for CH₄ Combustion

G. PECCHI, P. REYES, R. ZAMORA, T. LÓPEZ and R. GÓMEZ, *J. Chem. Technol. Biotechnol.*, 2005, 80, (3), 268–272

Pd–CeO₂-supported catalysts, prepared by the sol-gel technique, were used for the catalytic combustion of CH_4 . The addition of CeO₂ to Al_2O_3 gave a highly dispersed catalyst when compared with their ZrO₂ counterparts. However, the catalytic activity of the Pd–CeO₂–ZrO₂ series is higher, due to the Pd having a larger particle size.

The Oxidation of Water by Cerium(IV) Catalysed by Nanoparticulate RuO₂ on Mesoporous Silica

N. C. KING, C. DICKINSON, W. ZHOU and D. W. BRUCE, *Dalton Trans.*, 2005, (6), 1027–1032

Mesoporous silicates were prepared by templating on the hexagonal mesophase of bis(2,2'-bipyridine)(4,4'-dionadecyl-2,2'-bipyridine)ruthenium(II) dichloride using liquid-crystal templating. On calcination, the surfactant template was removed, except for the central Ru ion that was oxidised to RuO₂ nanoparticles (1) within the pores. (1) were active in catalysing the oxidation of H₂O by acidic Ce^{IV}.

HOMOGENEOUS CATALYSIS

Pd Nanoparticle Aging and Its Implications in the Suzuki Cross-Coupling Reaction

J. HU and Y. LIU, *Langmuir*, 2005, 21, (6), 2121–2123

The Pd nanoparticles (1) recovered from the N,N -dihexylcarbodiimide–Pd nanoparticle composite catalysts used in Suzuki cross-couplings, were found to transform from spherical-shape to larger needle-shaped crystals. (1) aggregated into nanosized blackberry-like assemblies (100–200 nm) as a result of Ostwald ripening. In a second type of ripening, atomic rearrangement occurred and (1) transformed into needle-shaped nanocrystals. These observations will be important for the future design and optimisation of durable nanoparticle catalysts.

Pd(II)-Biquinoline Catalyzed Aerobic Oxidation of Alcohols in Water

B. P. BUFFIN, J. P. CLARKSON, N. L. BELITZ and A. KUNDU, *J. Mol. Catal. A: Chem.*, 2005, 225, (1), 111–116

$\text{Pd}(\text{OAc})_2$ stabilised by 2,2'-biquinoline-4,4'-dicarboxylic acid was used in the aerobic oxidation of primary and secondary alcohols. H₂O was used as the reaction solvent, with air as the oxidant. Aliphatic primary alcohols were fully oxidised to carboxylic acid products. Secondary alcohols gave the corresponding ketones. The catalyst can be recycled.

New Carbazole–Oxadiazole Dyads for Electroluminescent Devices: Influence of Acceptor Substituents on Luminescent and Thermal Properties

K. R. J. THOMAS, J. T. LIN, Y.-T. TAO and C.-H. CHUEN, *Chem. Mater.*, 2004, 16, (25), 5437–5444

Oxadiazole-incorporated carbazoylamines (1) were synthesised using Pd catalysed C–N coupling reactions with $\text{Pd}(\text{dba})_2/\text{P}(t\text{-Bu})_3$ catalyst and $t\text{-BuONa}$ base. The reactions were best carried out in toluene at 80°C. Yields of (1) ranged from 75–95%. (1) were purified by reprecipitating twice from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ before application in the electroluminescent devices, such as OLEDs.

Hydroformylation of 1-Hexene in Ionic Liquids Catalyzed by Highly Active Rhodium-Phosphine Complexes

H. ZHENG, M. LI, H. CHEN, R. LI and X. LI, *Chin. J. Catal.*, 2005, 26, (1), 4–6

The hydroformylation of 1-hexene catalysed by $\text{HRh}(\text{CO})(\text{TPPTS})_3$ complexes (1) (TPPTS = triphenylphosphine-*m*-trisulfonic acid trisodium salt) was carried out in 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{bmim}]\text{BF}_4$). The activity and selectivity of (1) in $[\text{bmim}]\text{BF}_4$ were higher than those in other ionic liquids. The TOF of 1-hexene and selectivity for aldehyde were 1508 h^{-1} and 92%, respectively, under optimum conditions. The high activity of (1) is due to its higher solubility in $[\text{bmim}]\text{BF}_4$ and to the absence of halide ions.

Mononuclear Ruthenium Catalysts for the Direct Propargylation of Heterocycles with Propargyl Alcohols

E. BUSTELO and P. H. DIXNEUF, *Adv. Synth. Catal.*, 2005, 347, (2–3), 393–397

While [(*p*-cymene)RuCl(PR₃)]⁺[OTf]⁻ (PR₃) (PR₃ = PCy₃, PPh₃) catalyse the propargylation of furan or 2-methylfuran by the alkynol HC≡CCH(OH)Ph in moderate yield, [(*p*-cymene)RuCl(CO)(PR₃)]⁺[OTf]⁻ are more active. The stoichiometric reaction of [(*p*-cymene)RuCl(PR₃)]⁺[B(Ar_F)₄]⁻ (Ar_F = 3,5-(CF₃)₂C₆H₃) and the alkynol resulted in the *in situ* formation, *via* allenylidene and hydroxycarbene intermediates, of [(*p*-cymene)RuCl(CO)(PR₃)]⁺[B(Ar_F)₄]⁻.

An Efficient Catalytic Asymmetric Route to 1-Aryl-2-imidazol-1-yl-ethanols

I. C. LENNON and J. A. RAMSDEN, *Org. Process Res. Dev.*, 2005, 9, (1), 110–112

Catalytic asymmetric transfer hydrogenation of 1-aryl-2-imidazol-1-yl-ethanones with formic acid using [(*R,R*)-T_sDPEN]Ru(Cymene)Cl gave homochiral 1-aryl-2-imidazol-1-yl-ethanols. The hydrogenation was carried out under mild conditions at a molar substrate-to-catalyst ratio of 1000–2000. Bisphosphino Ru diamine complexes were found to be ineffective.

FUEL CELLS

High-Temperature Polymer Electrolytes for PEM Fuel Cells: Study of the Oxygen Reduction Reaction (ORR) at a Pt–Polymer Electrolyte Interface

Z. LIU, J. S. WAINRIGHT and R. F. SAVINELL, *Chem. Eng. Sci.*, 2004, 59, (22–23), 4833–4838

A micro-band electrode cell was used to investigate the ORR for a Pt/polybenzimidazole–phosphoric acid system. The obtained Tafel plots were linear over four orders of magnitudes of kinetic current density. Both the kinetic parameters and the mass transport data were comparable to those of a Pt/phosphoric acid system.

Effects of Preparation Conditions on Performance of Carbon-Supported Nanosize Pt-Co Catalysts for Methanol Electro-Oxidation under Acidic Conditions

J. ZENG and J. Y. LEE, *J. Power Sources*, 2005, 140, (2), 268–273

Pt/C and Pt-Co/C were prepared by NaBH₄ reduction of metal precursors. Citric acid was used as the complexing agent. The largest Pt-Co particles (12 nm) were formed in alkaline solution and the smallest particles (3.7 nm) in unbuffered solution. XPS showed that Pt is in the metallic state, whereas most of the Co is oxidised. The performance of the Pt-Co/C catalysts in MeOH electrooxidation under acidic conditions showed improvements over the Pt/C catalyst in both activity and CO-tolerance due to the Co addition.

Catalytic Activity of Pt–Ru Alloys Synthesized by a Microemulsion Method in Direct Methanol Fuel Cells

L. XIONG and A. MANTHIRAM, *Solid State Ionics*, 2005, 176, (3–4), 385–392

A microemulsion method was used to prepare nanostructured Pt-Ru/C catalysts (1) with different particle sizes. The electrochemical performances of (1) were evaluated in half cells with a mixture of 1 M H₂SO₄ and 1 M MeOH and in single cell DMFCs. (1) prepared with a water to surfactant molar ratio (*W*) of 10 exhibited the maximum mass activity with the least charge transfer resistance at an optimum particle size of ~ 5.3 nm. The mass activity decreases and the charge transfer resistance increases as the value of *W* decreases or increases from 10.

The Behavior of Palladium Catalysts in Direct Formic Acid Fuel Cells

Y. ZHU, Z. KHAN and R. I. MASEL, *J. Power Sources*, 2005, 139, (1–2), 15–20

Pd-based anode catalysts were used in DFAFCs. Power densities of 255 to 230 mW cm⁻² were achieved at relatively high voltages of 0.40 to 0.50 V in formic acid (3.0 to 15.0 M) at 20°C. A MEA with a Pd catalyst gave some decay in fuel cell performance over several hours. However, the performance can be completely recovered by applying a positive potential at the anode.

ELECTRICAL AND ELECTRONIC ENGINEERING

On the Perpendicular Anisotropy of Co/Pd Multilayers

J. I. HONG, S. SANKAR, A. E. BERKOWITZ and W. F. EGELHOFF, *J. Magn. Magn. Mater.*, 2005, 285, (3), 359–366

Co/Pd multilayers were deposited both at room temperature when thermally activated interfacial intermixing augmented the intentional alloying, and at 77 K. Stressed interfacial alloying is the dominant mechanism. Low temperature measurements indicated the presence of polarised Pd. The hard-axis magnetisation was modelled with a distribution of local perpendicular anisotropies which reflect local composition variations.

Synthesis and Characterization of CaRuO₃ and SrRuO₃ for Resistor Paste Application

K. GURUNATHAN, N. VYAWAHARE and D. P. AMALNERKAR, *J. Mater. Sci.: Mater. Electron.*, 2005, 16, (1), 47–53

Ca and Sr ruthenates (1) were prepared by air heating admixtures of the respective carbonates of Ca/Sr and RuO₂ at 500, 800 and 900°C for 15 h. The solid-state reactions occurred at 700–800°C. These powders still contained carbonate and hence were heated again at 900°C for 15 h to eliminate the carbonate. The average particle size of (1) is ~ 200–400 nm. The resistor paste was formulated using (1) prepared at 800 or 900°C and heat treated at 900°C.