

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Determination of Diffusion Coefficient of Hydrogen in Metals and Their Elastic Modulus by Generalised Impedance

P. ZOLTOWSKI and B. LEGAWIEC, *J. Electroanal. Chem.*, 2004, 572, (2), 205–210

Transport of H in elastic metals has been analysed in terms of an impedance-like non-linear transfer function (TF). The equilibrium in a membrane was perturbed by application of a sinusoidal signal of concentrations of H, of large amplitude, to a surface. The fundamental harmonics of periodically reproducible flux at this surface is considered as the response. The TF is defined as the ratio of the signal to the response. The TF was used in determining the diffusion coefficient of H in α -phase Pd-H and Pd₈₁Pt₁₉-H, and their bulk elastic moduli.

Gas Loading of Deuterium in Palladium at Low Temperature

F. SCARAMUZZI, *J. Alloys Compd.*, 2004, 385, (1–2), 19–27

An experimental technique that can be used to measure the absorption of H or D gas in a thin Pd sample (1) at low temperature is described. For D, the results consisted of measurements of the equilibrium loading ratio, X , as a function of pressure, on (1) 3.6 μm thick at 150 K. Values of $X \leq 1$ were measured at pressures of < 1 bar. The electrical resistance of (1) was measured as function of temperature and X .

Effect of Hydrogen on the Electrical Resistance of Melt-Spun Mg₉₀Pd₁₀ Amorphous Alloy

S. NAKANO, S. YAMAURA, S. UCHINASHI, H. KIMURA and A. INOUE, *Sens. Actuators B: Chem.*, 2005, 104, (1), 75–79

The electrical resistance of the title alloy (1) increased after electrochemical H charging and decreased after H discharging in 6 N KOH solution. The electrical resistance of (1) immersed in H-dissolved H₂O increased with immersion time and the increase was dependent on the H concentration in the H₂O. (1) may find use as a H sensor in H₂O.

CHEMICAL COMPOUNDS

A High-Pressure and High-Temperature Synthesis of Platinum Carbide

S. ONO, T. KIKEGAWA and Y. OHISHI, *Solid State Commun.*, 2005, 133, (1), 55–59

Pt carbide (1) was synthesised using high pressure and high temperature in a laser-heated diamond anvil cell. (1) has a rock-salt type structure, with space group $Fm\bar{3}m$ and cubic symmetry. (1) remains stable to ≤ 120 GPa. After decompression, the new high-pressure phase was recoverable at ambient pressure.

Cyclometalated Tridentate C-N-N Ligands with an Amine or Amido Donor in Platinum(II) and Palladium(II) Complexes and a Novel Potassium Alkoxide Aggregate

D. SONG and R. H. MORRIS, *Organometallics*, 2004, 23, (19), 4406–4413

2-Phenyl-6-(2-aminoisopropyl)pyridine (papH₂) was used to prepare Pt(papH)Cl (1) and Pd(papH)Cl. In both complexes the $\kappa^3\text{N}_2\text{N}_2\text{C}$ tridentate papH formed two five-membered rings with the metal, one of which was created by cyclometallation of the *ortho* C of the phenyl group. (1) reacted with KO^tBu to give [Pt(pap)]₂(KCl)(KO^tBu)₈ (2). The novel structure of (2) involves two Pt(pap) moieties being attached to the K₉O₈Cl “core” of the K alkoxide aggregate.

Purine-Based Carbenes at Rhodium and Iridium

J. SCHÜTZ and W. A. HERRMANN, *J. Organomet. Chem.*, 2004, 689, (19), 2995–2999

Purine-based carbenes were attached to Rh and Ir through the *in situ* deprotonation of the respective azolium salts. Trimethyloxonium tetrafluoroborate was reacted with caffeine to give 1,3,7,9-tetramethylxanthinium tetrafluoroborate. The salt and 7,9-dimethylhypoxanthinium iodide were used as a consecutive precursor to form Rh (I) and Ir (I) carbenes, [M(L)(L_{Carbene})₂]I and M(L)(L_{Carbene})(I) (where M = Rh, Ir; L_{Carbene} = 1,3,7,9-tetramethylxanthine-8-ylidene, 7,9-tetramethylhypoxanthine-8-ylidene; L = η^4 -1,5-COD, CO).

On the Silicides EuIr₂Si₂ and Lu₅Si₃

U. CH. RODEWALD, B. HEYING, D. JOHRENDT and R. PÖTTGEN, *Z. Naturforsch.*, 2004, 59b, (9), 969–974

EuIr₂Si₂ (1) was synthesised from the elements in a sealed Ta tube in a H₂O-cooled sample chamber of an induction furnace. Lu₅Si₃ was obtained by arc-melting of the elements. The Ir and Si atoms in (1) build up a 3D [Ir₂Si₂] network with Ir–Si and Si–Si interactions. The Eu atoms fill cages within the network.

High-Pressure Synthesis of Metallic Perovskite Ruthenate CaCu₃Ga₂Ru₂O₁₂

S.-H. BYEON, S.-S. LEE, J. B. PARISE, P. M. WOODWARD and N. H. HUR, *Chem. Mater.*, 2004, 16, (19), 3697–3701

CaCu₃Ga₂Ru₂O₁₂ (1) was synthesised at 12.5 GPa and 1200°C and recovered to room pressure and temperature conditions. In (1) the Ga and Ru cations in the perovskite-like structure are disordered over the octahedral sites. Magnetic susceptibility (at 5–300 K in an applied magnetic field of 5 kG) and electrical resistivity (at 10–400 K) measurements showed that (1) is a Pauli-paramagnetic conductor. (1) shows metallic conductivity in a perovskite-type oxide that contains the Ru(V) oxidation state.

ELECTROCHEMISTRY

Electrochemical Quartz Crystal Nanobalance to Detect Solvent Displacement by pH-Induced Conformational Changes of Proteins at Pt

N. P. COSMAN and S. G. ROSCOE, *Anal. Chem.*, 2004, 76, (19), 5945–5952

The adsorption behaviour of the proteins holo- and apo- α -lactalbumin at a Pt electrode (1) was studied in electrolyte solutions of pH < 2, 7.4 and 11 at 298 K. Electrochemical quartz crystal nanobalance frequency measurements gave a measure of nanogram changes on (1) due to solvent displacement by the adsorbed protein. Simultaneous CV charge transfer measurements gave protein surface concentration.

Solvent Effects on Charge Transport through Solid Deposits of [Os(4,4'-diphenyl-2,2'-dipyridyl)₂Cl₂]

R. J. FORSTER, J. IQBAL, J. HJELM and T. E. KEYES, *Analyst*, 2004, 129, (12), 1186–1192

Mechanically attached, solid-state films (1) of the title complex were formed on Au macro- and micro-electrodes. The voltammetric response of (1) associated with the Os^{2+/3+} redox reaction is similar of that observed for an ideal reversible, solution phase redox couple when the contacting electrolyte contains 40% v/v of MeCN. Preferential solvation of the redox centres by MeCN allows the incorporation of charge compensating counterions.

PHOTOCONVERSION

Triplet Exciton Diffusion and Delayed Interfacial Charge Separation in a TiO₂/PdTPPC Bilayer: Monte Carlo Simulations

J. E. KROEZE, T. J. SAVENIJE, L. P. CANDEIAS, J. M. WARMAN and L. D. A. SIEBBELES, *Sol. Energy Mater. Sol. Cells*, 2005, 85, (2), 189–203

Nanosecond photoexcitation of a bilayer of anatase TiO₂ coated with Pd tetrakis(4-carboxyphenyl)porphyrin (1) causes a delayed after-pulse growth in the conductivity over many μ s. The slow diffusion of (1) triplet excitons was followed by electron injection into the TiO₂ conduction band. Monte Carlo calculations of the exciton diffusion and exciton-exciton annihilation describe the experimentally observed temporal form and intensity dependence.

Amphiphilic Polypyridyl Ruthenium Complexes with Substituted 2,2'-Dipyridylamine Ligands for Nanocrystalline Dye-Sensitized Solar Cells

P. WANG, R. HUMPHRY-BAKER, J. E. MOSER, S. M. ZAKEERUDDIN and M. GRÄTZEL, *Chem. Mater.*, 2004, 16, (17), 3246–3251

Ru(dcbpy)(L)(NCS)₂ dye (dcbpy = 4,4'-dicarboxylic acid-2,2'-bipyridine; L = N,N-di(2-pyridyl)-dodecylamine or N,N-di(2-pyridyl)-tetradecylamine) can be used as solar cell sensitizers. Efficiencies of 8.2% at the 100 mW cm⁻² irradiance of air mass 1.5 solar light and \geq 8.7% at lower light intensities were achieved.

APPARATUS AND TECHNIQUE

Ethanol Gas Sensing Properties of Nano-Crystalline Cadmium Stannate Thick Films Doped with Pt

Y.-L. LIU, Y. XING, H.-F. YANG, Z.-M. LIU, Y. YANG, G.-L. SHEN and R.-Q. YU, *Anal. Chim. Acta*, 2004, 527, (1), 21–26

Pt (0.1–2 at.%) was incorporated into nanocrystalline CdSnO₃ (1) by the impregnation technique. Conductance responses of thick films of (1) were measured after exposure to EtOH, CO, CH₄, C₄H₁₀, gasoline and LPG at different operating temperatures. Sensors doped with Pt had good sensitivity and selectivity to EtOH vapour. The optimum sensitivity was obtained when (1) was doped with 1.5 at.% Pt.

All-Optical Hydrogen-Sensing Materials Based on Tailored Palladium Alloy Thin Films

Z. ZHAO, Y. SEVRYUGINA, M. A. CARPENTER, D. WELCH and H. XIA, *Anal. Chem.*, 2004, 76, (21), 6321–6326

The phase-dependent H time response characteristics of 20 nm thick Pd-Au (Ag) films (1) were investigated via optical reflectance measurements. They displayed a strong dependence on the α , mixed α/β and β Pd-hydride phases formed in (1). The response time peaks in the $\alpha \rightarrow \beta$ phase transition region were 1625 s at 0.4% H₂ for Pd_{0.94}Ag_{0.06} and 405 s at 1% H₂ for Pd_{0.94}Au_{0.06}. The addition of Au (up to 40%) shifted and then inhibited the $\alpha \rightarrow \beta$ phase transition region. Pd_{0.6}Au_{0.4} was above the critical isotherm threshold for undergoing a phase transition and had response time < 50 s.

HETEROGENEOUS CATALYSIS

Parallel IR Spectroscopic Characterization of CO Chemisorption on Pt Loaded Zeolites

P. KUBANEK, H.-W. SCHMIDT, B. SPLIETHOFF and F. SCHÜTH, *Microporous Mesoporous Mater.*, 2005, 77, (1), 89–96

Parallel characterisation of Pt-containing zeolites ZSM-5 and Y was achieved using FTIR spectroscopy in transmission mode combined with a focal plane array detector. The Pt species in the zeolite were investigated using the chemisorption of CO. The 8-fold degree of parallelisation lowered the total time required for data collection.

Conversion of Halon 1211 (CBrClF₂) over Supported Pd Catalysts

H. YU, E. M. KENNEDY, MD. A. UDDIN, A. A. ADESINA and B. Z. DLUGOGORSKI, *Catal. Today*, 2004, 97, (2–3), 205–215

The conversion of halon 1211 was investigated over γ -Al₂O₃ and 0.5% Pd supported on Al₂O₃, fluorinated Al₂O₃, AlF₃, and Al₂O₃ pretreated with CH₄ and CHClF₂, at 443–523 K. The Pd was transformed to Pd carbide in the CH₄ treated Pd/Al₂O₃, but not in the CHClF₂ treated Pd/Al₂O₃ (Al₂O₃ was partially fluorinated). In the absence of H₂, the conversion of halon 1211 over Al₂O₃ and Pd/Al₂O₃ gave a similar product profile and the reactions follow a heterogeneous halogen exchange reaction pathway.

Heck Reaction Catalyzed by Nanosized Palladium on Chitosan in Ionic Liquids

V. CALÒ, A. NACCI, A. MONOPOLI, A. FORNARO, L. SABBATINI, N. CIOFFI and N. DITARANTO, *Organometallics*, 2004, 23, (22), 5154–5158

Pd nanoparticles/chitosan (1) was very effective for the Heck reaction of aryl bromides and activated aryl chlorides in tetrabutylammonium bromide with tetrabutylammonium acetate as base. Conversion of bromobenzene or *p*-nitrochlorobenzene into cinnamates took only 15 min. The Pd colloids are stabilised by the solvent. Any PdH is readily neutralised by the base. (1) can be recycled.

One-Pot Synthesis of Recyclable Palladium Catalysts for Hydrogenations and Carbon–Carbon Coupling Reactions

N. KIM, M. S. KWON, C. M. PARK and J. PARK, *Tetrahedron Lett.*, 2004, 45, (38), 7057–7059

Pd nanoparticles (1) were prepared from Pd(PPh₃)₄ in tetra(ethylene glycol) and Si(OMe)₄ (or Ti(O^{*i*}Pr)₄). (1) were then encapsulated in SiO₂ (or TiO₂) matrix by treatment with H₂O. SiO₂ (or TiO₂)/TEG/Pd showed high catalytic activity in alkene and alkyne hydrogenations and in Suzuki–Miyaura, Sonogashira, Heck–Mizoroki and Stille reactions.

Surface Study of Rhodium Nanoparticles Supported on Alumina

A. MAROTO-VALIENTE, I. RODRÍGUEZ-RAMOS and A. GUERRERO-RUIZ, *Catal. Today*, 2004, 93–95, 567–574

Rh nanoparticles (1 and 3 wt.%) / Al₂O₃ were studied by H₂ and CO adsorption microcalorimetry and by IR spectroscopy of the chemisorbed CO. The *n*-butane hydrogenolysis reaction test was employed to examine surface sites. The energetic distribution of surface sites depended slightly on the metal loading and can be modified by the pretreatment conditions. Partially reduced Rh atoms stabilised by Cl ions remaining from the precursor were found. The increased density on Rh (111) planes on 3 wt.% Rh/Al₂O₃ treated with H₂O enhanced both activity for the hydrogenolysis and selectivity towards ethane.

HOMOGENEOUS CATALYSIS

Palladium-Catalyzed Addition of Mono- and Dicarboxyl Compounds to Conjugated Dienes

A. LEITNER, J. LARSEN, C. STEFFENS and J. F. HARTWIG, *J. Org. Chem.*, 2004, 69, (22), 7552–7557

An intermolecular addition of the α -C–H bond of monocarbonyl and 1,3-dicarbonyl compounds to dienes was achieved in high yields using a catalyst generated *in situ* from CpPd(allyl) (1) and 1,3-bis(dicyclohexylphosphino)propane. The common additions of cyanoesters, malonitrile and α -sulfonyl esters readily took place; unusual additions of ketones, lactones, esters and nitriles were also possible. The first enantioselective version of this reaction was achieved using (1) and a Josiphos ligand with \leq 81% ee.

General and Efficient Methodology for the Suzuki–Miyaura Reaction in Technical Grade 2-Propanol

O. NAVARRO, Y. OONISHI, R. A. KELLY, E. D. STEVENS, O. BRIEL and S. P. NOLAN, *J. Organomet. Chem.*, 2004, 689, (23), 3722–3727

Pd *N*-heterocyclic carbenes or phosphines were investigated in the Suzuki–Miyaura reaction using technical grade 2-propanol (1) as solvent and K *t*-butoxide as base. The cross-coupling of electron-rich aryl chlorides with sterically hindered aryl boronic acids gave di- and tri-*ortho*-substituted biaryls in short times. (1) did not require pre-drying or purification.

Palladium-Catalyzed Intramolecular α -Arylation of Aliphatic Ketone, Formyl, and Nitro Groups

H. MURATAKE, M. NATSUME and H. NAKAI, *Tetrahedron*, 2004, 60, (51), 11783–11803

PdCl₂(Ph₃P)₂–Cs₂CO₃ was used for the intramolecular arylation of substrates bearing a ketone, formyl or nitro terminating group to give carbocyclics. Arylation of the ketones gave benzene-annulated bridged or spirocycloalkanone derivatives, depending on the type of cyclisation precursors. Arylation in formyl compounds occurred in the α -position or at the carbonyl C depending on the type of cyclisation precursors and on the solvent. An α -arylated secondary nitro group was partially transformed to ketone, whereas a tertiary nitro group was partially eliminated to afford a styrene-type olefin.

Successful Development and Scale-up of a Palladium-Catalysed Amination Process in the Manufacture of ZM549865

G. E. ROBINSON, O. R. CUNNINGHAM, M. DEKHANE, J. C. MCMANUS, A. O'KEARNEY-MCMULLAN, A. M. MIRAJKAR, V. MISHRA, A. K. NORTON, B. VENUGOPALAN and E. G. WILLIAMS, *Org. Process Res. Dev.*, 2004, 8, (6), 925–930

Pd-catalysed amination and ester hydrolysis has been used to synthesise a key intermediate in the manufacture of ZM549865 (a 5-HT receptor antagonist). Pd dibenzylideneacetone was employed for the amination of ethyl 8-bromo-6-fluoro-4-oxo-4*H*-2-chromenecarboxylate. Amination at 125°C instead of 80°C and optimising the reaction conditions increased the overall yield from 44% to \sim 70% and reduced the reaction time from days to hours.

A Convenient Synthesis of High-Loaded Palladium(II) ROMP Polymers

D. C. BRADDOCK, D. CHADWICK and E. LINDNER-LÓPEZ, *Tetrahedron Lett.*, 2004, 45, (49), 9021–9024

A method for the immobilisation of two *O,O'*-chelate Pd(II) complexes via ROMP has been established. The monomer bis[1-(5-norbornen-2-yl)butan-1,3-dionato]palladium(II) (1) was readily prepared from 5-acetoacetyl-2-norbornene and Na₂PdCl₄. (1) underwent ROMP under mild conditions to give a highly-loaded Pd(II)-containing polymer (Pd, 23 wt.%).

Rhodium(II)-Catalyzed Aziridination of Allyl-Substituted Sulfonamides and Carbamates

A. PADWA, A. C. FLICK, C. A. LEVERETT and T. STENGEL, *J. Org. Chem.*, 2004, 69, (19), 6377–6386

Unsaturated sulfonamides underwent intramolecular aziridination in the presence of $\text{PhI}(\text{OAc})_2$, MgO and $\text{Rh}_2(\text{OAc})_4$ to give bicyclic aziridines in excellent yield. The resulting azabicyclic sulfonamides with the addition of *p*-TsOH in MeOH underwent exclusive opening of the aziridine ring at the most substituted position giving six- and seven-membered ring products in high yield.

Iridium-Catalyzed Hydroboration of Alkenes with Pinacolborane

Y. YAMAMOTO, R. FUJIKAWA, T. UMEMOTO and N. MIYAURA, *Tetrahedron*, 2004, 60, (47), 10695–10700

$\text{Ir}(\text{I})$ phosphine complexes (1) are excellent catalysts for room temperature hydroboration of terminal and internal alkenes possessing an aliphatic or aromatic substituent on the vinylic C with pinacolborane. $[\text{Ir}(\text{cod})\text{Cl}]_2/2\text{dppm}$ was the best catalyst system for hydroboration of aliphatic terminal and internal alkenes at room temperature; addition of the B atom to the terminal C of 1-alkenes was achieved with > 99% selectivity. For vinylarenes such as styrene, $[\text{Ir}(\text{cod})\text{Cl}]_2/2\text{dppe}$ gave the best yields. (1) exhibited higher levels of catalyst activity and selectivity than the corresponding Rh complexes.

FUEL CELLS

Preparation and Characterization of Carbon Supported Pt and PtRu Alloy Catalysts Reduced by Alcohol for Polymer Electrolyte Fuel Cell

T. KIM, M. TAKAHASHI, M. NAGAI and K. KOBAYASHI, *Electrochim. Acta*, 2004, 50, (2–3), 813–817

Highly dispersed fine Pt and PtRu alloy particles on C support were prepared by a simple alcohol-reduction method using polyvinylpyrrolidone as a stabiliser. Highly uniform nanoparticles were obtained. The structure and morphology of the catalysts could be readily controlled. The catalysts showed promising activity in O reduction and MeOH oxidation.

Methanol Electro-Oxidation and Direct Methanol Fuel Cell Using Pt/Rh and Pt/Ru/Rh Alloy Catalysts

J.-H. CHOI, K.-W. PARK, I.-S. PARK, W.-H. NAM and Y.-E. SUNG, *Electrochim. Acta*, 2004, 50, (2–3), 783–786

The title catalysts (1) for application in DMFCs were prepared by a borohydride reduction method combined with freeze drying. (1) had specific surface areas of $\sim 65\text{--}75\text{ m}^2\text{ g}^{-1}$. XRD patterns established that (1) were well alloyed and the average size of (1) was confirmed by TEM. (1) of composition Pt/Rh (2:1) and Pt/Ru/Rh (5:4:1) had better catalytic activities for MeOH electrooxidation than Pt or Pt/Ru (1:1), respectively.

Performance of Methanol Oxidation Catalysts with Varying Pt:Ru Ratio as a Function of Temperature

A. J. DICKINSON, L. P. L. CARRETTE, J. A. COLLINS, K. A. FRIEDRICH and U. STIMMING, *J. Appl. Electrochem.*, 2004, 34, (10), 975–980

At 25°C, a Pt-rich 3:2 Pt:Ru atomic ratio DMFC-type catalyst was more active for MeOH oxidation than a 1:1 catalyst. Only the Pt is active towards MeOH dehydrogenation, as this process requires high thermal activation on Ru sites. At 65°C, the 1:1 catalyst gave much higher currents across the entire polarisation range. At 45°C, the 3:2 catalyst is better at lower current values, while the 1:1 catalyst is superior at higher current densities.

MEDICAL USES

Synthesis and DNA-Binding Properties of Binuclear Platinum Complexes with Two *trans*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}]^+$ Units Bridged by 4,4'-Dipyridyl Sulfide or Selenide

G. ZHAO, X. HU, P. YU and H. LIN, *Transition Met. Chem.*, 2004, 29, (6), 607–612

$\{trans\text{-}[\text{Pt}(\text{NH}_3)_2\text{Cl}]_2(\text{dpsu})\}(\text{NO}_3)_2$ (1) and $\{trans\text{-}[\text{Pt}(\text{NH}_3)_2\text{Cl}]_2(\text{dpse})\}(\text{NO}_3)_2$ (dpsu = 4,4'-dipyridyl sulfide; dpse = 4,4'-dipyridyl selenide) were prepared for use as potential antitumour agents. Compared with $[cis\text{-Pt}(\text{NH}_3)_2\text{Cl}(4\text{-methylpyridine})]\text{NO}_3$, (1) exhibits an almost two-fold stronger DNA-binding ability. (1) may bind bifunctionally to DNA.

Synthesis, Characterization, and Cytotoxicities of Palladium(II) and Platinum(II) Complexes Containing Fluorinated Pyridinecarboxaldimines

S. J. SCALES, H. ZHANG, P. A. CHAPMAN, C. P. MCRORY, E. J. DERRAH, C. M. VOGELS, M. T. SALEH, A. DECKEN and S. A. WESTCOTT, *Polyhedron*, 2004, 23, (13), 2169–2176

The condensation of 2-pyridinecarboxaldehyde with primary amines containing F groups gave the corresponding pyridinecarboxaldimine ligands ($\text{N-N}'$). Addition of these ligands to $[\text{MCl}_2(\text{coe})_2]$ ($\text{M} = \text{Pt}, \text{Pd}$; $\text{coe} = cis\text{-cyclooctene}$) gave $cis\text{-MCl}_2(\text{N-N}')$ (1) in moderate to high yields. Cytotoxicities of (1) were investigated against OV2008 (human ovarian carcinoma) and the analogous cisplatin-resistant C13.

The Potential Use of Rhodium N-Heterocyclic Carbene Complexes as Radiopharmaceuticals: The Transfer of a Carbene from Ag(I) to $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$

C. A. QUEZADA, J. C. GARRISON, M. J. PANZNER, C. A. TESSIER and W. J. YOUNGS, *Organometallics*, 2004, 23, (21), 4846–4848

The first reported N-heterocyclic carbene transfer from Ag(I) to $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ was used to prepare two new Rh N-heterocyclic carbenes (1). The syntheses were carried out in DMSO at 100°C for 1 h. The very high stability of (1) indicates that ^{103}Rh complexes of bisimidazole ligands with targeting substituents such as peptides may be used for radiation therapy.