

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Effect of Hydrogen-Sulfide on the Hydrogen Permeance of Palladium-Copper Alloys at Elevated Temperatures

B. D. MORREALE, M. V. CIOCCO, B. H. HOWARD, R. P. KILLMEYER, A. V. CUGINI and R. M. ENICK, *J. Membrane Sci.*, 2004, **241**, (2), 219–224

The H permeance of Pd-Cu foils (1) (0.1 mm thick) was evaluated using transient flux measurements over 603–1123 K and pressures \leq 620 kPa, in the presence and absence of 1000 ppm H₂S. S resistance (no significant change in permeance) was correlated with the temperatures associated with f.c.c. (1). The H permeance of b.c.c. (1) was up to two orders of magnitude lower on exposure to H₂S. A smooth transition from S poisoning to S resistance with increasing temperature was correlated with the b.c.c. to f.c.c. transition.

Magnetism of CaRuO₃ Crystal

A. KORIYAMA, M. ISHIZAKI, T. C. OZAWA, T. TANIGUCHI, Y. NAGATA, H. SAMATA, Y. KOBAYASHI and Y. NORO, *J. Alloys Compd.*, 2004, **372**, (1–2), 58–64

The magnetic properties of polycrystalline (1) and single-crystal (2) samples of CaRuO₃ were studied. The $M(T)$ curves of (1) showed irreversible behaviour and the $M(H)$ curve showed weak ferromagnetic behaviour at < 60 K. The $M(H)$ curve of (2) exhibited peculiar behaviour at 1.7 and 5 K, showing evidence of magnetic order at very low temperature.

CHEMICAL COMPOUNDS

Insertion of Phenylacetylene into

[Pt(GeMe₃)(SnMe₃)(PMe₂Ph)₂]

T. SAGAWA, R. TANAKA and F. OZAWA, *Bull. Chem. Soc. Jpn.*, 2004, **77**, (7), 1287–1295

The reaction of Me₃GeSnMe₃ with a Pt(0) complex, *in situ* generated from [Pt(cod)₂] and PhMe₂Ph, gave a *cis-trans* mixture of [Pt(GeMe₃)(SnMe₃)(PMe₂Ph)₂] (1). Recrystallisation of crude (1) from CH₂Cl₂-pentane gave *cis*-(1). (1) underwent competitive insertion of phenylacetylene into the Pt-Sn and Pt-Ge bonds.

The Crystal Structure of [Pt(NH₃)₄][PtI₄]:

Comparison with Magnus' Green Salt

J. S. CASAS, Y. PARAJÓ, Y. ROMERO, A. SÁNCHEZ-GONZÁLEZ, J. SORDO and E. M. VÁZQUEZ-LÓPEZ, *Z. Anorg. Allg. Chem.*, 2004, **630**, (7), 980–982

The structure of [Pt(NH₃)₄][PtI₄] (1) was found to be isotopic with Magnus' green salt and is unchanged at low temperature except for a slight contraction of the unit cell. (1) consisted of [Pt(NH₃)₄]²⁺ and [PtI₄]²⁻; the Pt atoms are surrounded by 4 N or 4 I atoms in square-planar arrangements. At 173 K the intermolecular stacking interaction Pt-Pt was shortened.

N-Benzoylimido Complexes of Palladium.

Synthesis, Structural Characterisation and Structure-Reactivity Relationship

G. BESENYEI, L. PÁRKÁNYI, G. SZALONTAI, S. HOLLY, I. PÁPAI, G. KERESZTURY and A. NAGY, *Dalton Trans.*, 2004, (13), 2041–2050

Benzoyl azides, ArC(O)N₃ (Ar = phenyl or substituted phenyl), react with [Pd₂Cl₂(dppm)₂] (1) (dppm = bis(diphenylphosphino)methane) to give novel benzoylnitrene complexes, [Pd₂Cl₂(μ-NC(O)Ar)(dppm)₂]. The C₂P₂Pd₂ rings are chiral. Crystallographic and solution IR studies of the reaction of a series of *para*-substituted benzoyl azides with (1) showed that the reaction obeys the Hammett equation.

Iridium(III) and Rhodium(III) Cyclometalated Complexes Containing Sulfur and Selenium Donor Ligands

M.-K. LAU, K.-M. CHEUNG, Q.-F. ZHANG, Y. SONG, W.-T. WONG, I. D. WILLIAMS and W.-H. LEUNG, *J. Organomet. Chem.*, 2004, **689**, (14), 2401–2410

Reaction of [M(Buppy)₂Cl]₂ (M = Ir (1), Rh (2); BuppyH = 2-(4'-*tert*-butylphenyl)pyridine) with Na(Et₂NCS₂), K[S₂P(OMe)₂] and K[N(Ph₂PS)₂] gave monomeric [M(Buppy)₂S[±]S] (S[±]S = Et₂NCS₂, S₂P(OMe)₂, N(PPh₂S)₂). Treatment of (1) with Na[N(PPh₂Se)₂] gave [Ir(Buppy)₂{N(PPh₂Se)₂}]₂. Reaction of (1) and (2) with AgOTf followed by treatment with KSCN gave [M(Buppy)₂]₂(μ-SCN)₂.

Mixed Iridium(III) and Ruthenium(II) Polypyridyl Complexes Containing Poly(ε-caprolactone)-bipyridine Macroligands

V. MARIN, E. HOLDER, R. HOOGENBOOM and U. S. SCHUBERT, *J. Polym. Sci. A: Polym. Chem.*, 2004, **42**, (17), 4153–4160

Coordination of a poly(ε-caprolactone)-bipyridine macroligand to Ir(III) and Ru(II) precursor complexes yielded the title complexes. Both photophysical and electrochemical properties of the metal-containing polymers confirmed the formation of the tris-Ir(III) and tris-Ru(II) polypyridyl species.

ELECTROCHEMISTRY

The Electrochemistry of Gold-Platinum Alloys

H. MÖLLER and P. C. PISTORIUS, *J. Electroanal. Chem.*, 2004, **570**, (2), 243–255

Au-Pt electrodes are more active for ethylene glycol electrooxidation than either Pt or Au electrodes. The Au-Pt electrodes in the solid solution condition are more active than two-phase electrodes. More severe poisoning occurs during the first few cycles at the Au-Pt electrodes than at both the Pt or Au electrodes. Longer potential pulsing cleaning cycles are needed to remove the poisons at the Au-Pt electrodes.

PHOTOCONVERSION

Micelle-Mediated UV-Photoactivation Route for the Evolution of Pd_{core}-Au_{shell} and Pd_{core}-Ag_{shell}

Bimetallics from Photogenerated Pd Nanoparticles
M. MANDAL, S. KUNDU, S. K. GHOSH and T. PAL, *J. Photochem. Photobiol. A: Chem.*, 2004, 167, (1), 17–22

UV-photoactivation of aqueous PdCl₂ gave Pd nanoparticles (1) with narrow size distribution (~ 5 nm) in poly(oxyethylene)isooctyl phenyl ether micelles, TX-100, as reducing agent. The TX-100 also acted as a stabiliser. The bimetallic colloids (10–30 nm) with varying metal ratios were prepared by successive ion loading using a seed-mediated method where (1) act as seeds.

Electronic and Photophysical Properties of a Novel Phenol Bound Dinuclear Ruthenium Complex: Evidence for a Luminescent Mixed Valence State

T. E. KEYES, B. EVRARD, J. G. VOS, C. BRADY, J. J. MCGARVEY and P. JAYAWEEERA, *Dalton Trans.*, 2004, (15), 2341–2346

A dinuclear Ru(II) complex (1), bridged by 3-(2-phenol)-5-(pyridin-2-yl)-1,2,4-triazole, was prepared electrochemically. A weak intervalence charge transfer transition was observed. Upon oxidation of the O₂N moiety luminescence from (1) is reversibly switched on at 0.3 V and reversibly switched off by the application of 1.3 or 0 V.

ELECTRODEPOSITION AND SURFACE COATINGS

Microstructure and Mechanical Properties of Ir-Ta Coatings on Nickel-Base Single-Crystal Superalloy TMS-75

P. KUPPUSAMI, H. MURAKAMI and T. OHMURA, *J. Vac. Sci. Technol. A*, 2004, 22, (4), 1208–1217

Ir-Ta coatings (1) with 16.2, 23.9, 40.7 and 65.1 at.% Ta were deposited at 573 K on the Ni-base single crystal superalloy, TMS-75, by DC magnetron sputtering by selecting the ratio of the surface areas of the Ir and Ta targets. (1) had a nanocrystalline structure where crystallite size and rms roughness decreased with increase in Ta content. Young's modulus and hardness of the coatings generally decreased with the increase in Ta content. However, the hardness peaked in the 16.2–23.9 at.% Ta range, possibly due to Ir₃Ta formation.

Cathodic Electrodeposition of RuO₂ Thin Films from Ru(III)Cl₃ Solution

B.-O. PARK, C. D. LOKHANDE, H.-S. PARK, K.-D. JUNG and O.-S. JOO, *Mater. Chem. Phys.*, 2004, 87, (1), 59–66

RuO₂ films (1) of different thicknesses were cathodically deposited on Ti substrates under galvanostatic conditions from aqueous acidic Ru(III)Cl₃ solution. XRD and TEM established that (1) are nanocrystalline. SEM showed that (1) are porous and that surface morphology changes with film thickness.

HETEROGENEOUS CATALYSIS

Hydroisomerization of *n*-Heptane and *n*-Tetradecane over Pt/SAPO-11

F. ZHANG, C.-H. GENG, Z.-X. GAO and J.-L. ZHOU, *J. Fuel Chem. Technol. (Chin.)*, 2004, 32, (3), 340–345

Hydroisomerisation of *n*-heptane and *n*-tetradecane over Pt/SAPO-11 was carried out in a fixed-bed, down-flow reactor at 200°C ~ 420°C, 0.5 MPa and WHSV of 2.0 h⁻¹. High *n*-alkane conversion with 90% selectivity to isomers was achieved. Paraffin isomerisation may occur inside the SAPO-11 channels.

Pd-Catalyzed Heck Arylation of Cycloalkenes—Studies on Selectivity Comparing Homogeneous and Heterogeneous Catalysts

L. DJAKOVITCH, M. WAGNER, C. G. HARTUNG, M. BELLER and K. KOEHLER, *J. Mol. Catal. A: Chem.*, 2004, 219, (1), 121–130

Heck reactions of aryl bromides with cyclohexene and cyclopentene were catalysed by: Pd/C, Pd/SiO₂, Pd/MgO, Pd/Al₂O₃, Pd(0)/Z, Pd(II)/Z and [Pd(NH₃)₄]²⁺/Z (Z = NaY, HY or ZSM-5 zeolites); and Pd(OAc)₂/PPh₃, Pd₂(dba)₃·dba/PCy₃ and the {Pd[P(σ-C₆H₄CH₃)₂-(σ-C₆H₄CH₂)(CH₃CO₂)]₂} “palladacycle”. Dissolved molecular Pd species are involved in the Heck coupling for all of the catalysts. The dehalogenation mechanism involves the surface of solid Pd metal particles and radical processes.

Drastic Increase of Selectivity for H₂O₂ Formation in Direct Oxidation of H₂ to H₂O₂ over Supported Pd Catalysts Due to Their Bromination

V. R. CHOUDHARY, C. SAMANTA and A. G. GAIKWAD, *Chem. Commun.*, 2004, (18), 2054–2055

Pd catalysts have high activity for H₂O₂ decomposition which limits their use for formation of H₂O₂ from H₂. The incorporation of bromide anions (1.0 wt.%) into Pd supported on Al₂O₃, ZrO₂, SiO₂, H-β zeolite or Ga₂O₃ overcomes this. These catalysts were used for the direct oxidation of H₂ to H₂O₂ by O₂ (at room temperature) in 0.03 M H₃PO₄. A large increase in selectivity for H₂O₂ formation was accompanied by a large decrease in the H₂O₂ decomposition activity. The bromide anions change the electronic properties of the Pd.

Rietveld Refinement and Activity of CO Oxidation over Pd/Ce_{0.8}Zr_{0.2}O₂ Catalyst Prepared via a Surfactant-Assisted Route

J. A. WANG, L. F. CHEN, M. A. VALENZUELA, A. MONTOYA, J. SALMONES and P. DEL ANGEL, *Appl. Surf. Sci.*, 2004, 230, (1–4), 34–43

Ce_{0.8}Zr_{0.2}O₂ nanophases (1) were synthesised using a surfactant-assisted method. Structural refinement by the Rietveld method confirmed that many cationic lattice defects were formed in the crystals of (1). Pd/Ce_{0.8}Zr_{0.2}O₂ calcined at 873–1173 K exhibited a more stable catalytic activity for CO oxidation, and also performed a lower light-off temperature at cool start < 373 K, in comparison with Pd/CeO₂.

Drastic Enhancement of SCR of NO over Ir Catalyst through Formation of Metallic Iridium on Na-Zeolite

J. SHIBATA, H. YOSHIDA, A. SATSUMA and T. HATTORI, *Chem. Lett.*, 2004, 33, (7), 800–801

Ir/Na-zeolite catalysts (1) have excellent activity at 500 K for the SCR of NO in a He atmosphere also containing CO/H₂. Low loaded (1) (0.5 wt.% Ir) could be used. Ir L_{III}-edge XANES and CO₂-H₂ titration were carried out. The Ir forms a highly active metallic species with low oxidation; this Ir species is highly dispersed. Ir/Na-MOR mordenite zeolite has the highest activity.

Local Barrier Height of Ir/TiO₂ Model Catalysts

Y. MAEDA, T. AKITA, M. OKUMURA and M. KOHYAMA, *Jpn. J. Appl. Phys.*, 2004, 43, (7B), 4595–4598

Ir was deposited on TiO₂ (110)-(1×2) surfaces by vacuum evaporation to form Ir/TiO₂ model catalysts (1). The local barrier height (LBH) of (1) was measured using scanning tunnelling microscopy and compared with that of Au/TiO₂ catalyst. The Ir was oxidised to IrO₂ by annealing at 1073 K. The LBH of IrO₂ particles was almost the same as that of the TiO₂ support, while the LBH of Au particles was 0.3 eV larger. The charge transfer between IrO₂ and TiO₂ is small. Electrons are transferred from TiO₂ to Au.

HOMOGENEOUS CATALYSIS

Synthetic Applications of Oxime-Derived Palladacycles as Versatile Catalysts in Cross-Coupling Reactions

D. A. ALONSO, L. BOTELLA, C. NÁJERA and M. C. PACHECO, *Synthesis*, 2004, (10), 1713–1718

Palladacycles derived from 4,4'-dichlorobenzophenone and 4-hydroxyacetophenone oximes are efficient and versatile pre-catalysts for C–C bond coupling reactions. These coupling reactions include Mizoroki-Heck, Suzuki-Miyaura, Stille, Ullmann-type, Sonogashira, sila-Sonogashira, Glaser and acylation of alkynes under very low loading conditions. The high yielding reactions can be carried out in air using either organic or aqueous solvents.

Dioxygen-Promoted Regioselective Oxidative Heck Arylations of Electron-Rich Olefins with Arylboronic Acids

M. M. S. ANDAPPAN, P. NILSSON, H. VON SCHENCK and M. LARHED, *J. Org. Chem.*, 2004, 69, (16), 5212–5218

Heck arylations of electron-rich heteroatom-substituted olefins with arylboronic acids to give acyclic enamides were carried out using Pd(OAc)₂ with 2,9-dimethyl-1,10-phenanthroline (dmphen) as the catalyst system. The reactions were carried out under O₂. The dmphen ligand controls the internal regioselectivity and mediates a reoxidation of Pd(0) with O₂, thus allowing a low catalyst loading. Controlled microwave heating and increased O pressure were used to reduce the reaction time to 1 h.

Microwave Promoted Heck Reactions Using an Oligo(ethylene glycol)-Bound SCS Palladacycle under Thermomorphic Conditions

D. E. BERGBREITER and S. FURYK, *Green Chem.*, 2004, 6, (6), 280–285

Pd catalysed Heck couplings using an air-stable, H₂O-soluble oligo(ethylene glycol)-bound SCS palladacycle catalyst (1) and microwave irradiation gave cinnamic acid derivatives in < 1 h. Recycling of (1) was achieved using a 10% aqueous dimethylacetamide-heptane thermomorphic system that was biphasic during the catalyst recovery step.

The RuO₄-Catalysed Dihydroxylation, Ketohydroxylation and Mono Oxidation—Novel Oxidation Reactions for the Synthesis of Diols and α -Hydroxy Ketones

B. PLIETKER and M. NIGGEMANN, *Org. Biomol. Chem.*, 2004, 2, (17), 2403–2407

A study of RuO₄-catalysed oxidations of alkenes resulted in the development of the first RuO₄-catalysed ketohydroxylation of olefins. Mechanistic studies of both dihydroxylation and ketohydroxylation gave rise to the first regioselective catalytic monooxidation of *vic*-diols. When applied in a two-step sequence of asymmetric dihydroxylation and regioselective monooxidation, enantiopure α -hydroxy ketones were obtained.

FUEL CELLS

CO Tolerance of Commercial Pt and PtRu Gas Diffusion Electrodes in Polymer Electrolyte Fuel Cells

F. HAJBOLOURI, B. ANDREAS, G. G. SCHERER and A. WOKAUN, *Fuel Cells*, 2004, 4, (3), 160–168

The CO tolerance of Pt and PtRu anodes from E-Tek and Tanaka were examined in PEFCs using AC impedance spectroscopy along steady-state current-voltage curves. The Tanaka PtRu (40:60) anode is reported to have better CO tolerance under the selected operating conditions. The impedance spectra of the Tanaka PtRu anode did not show any inductive behaviour and its CO surface coverage was low.

Synthesis and Characterization of Methanol Tolerant Pt/TiO_x/C Nanocomposites for Oxygen Reduction in Direct Methanol Fuel Cells

L. XIONG and A. MANTHIRAM, *Electrochim. Acta*, 2004, 49, (24), 4163–4170

The title nanocomposites (1) were prepared by: depositing hydrated TiO₂ on Pt/C; reducing H₂PtCl₆ with Na formate on C-supported hydrated TiO₂ (TiO₂/C); and simultaneously depositing hydrated TiO₂ and reducing H₂PtCl₆ with Na formate on C support. (1) underwent heat treatment at 500 and 900°C in 90% Ar/10% H₂. Some of (1) had higher catalytic activity than Pt/C. (1) also exhibited better MeOH tolerance than Pt/C.