

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Reduction of Pt(II) by H₂: Effects of Citrate and NaOH and Reaction Mechanism

A. HENGLEIN and M. GIERSIG, *J. Phys. Chem. B*, 2000, 104, (29), 6767–6772

Aged aqueous PtCl₄²⁻ solutions are reduced by H₂ in the absence of a stabiliser and in the presence of stabilising Na citrate or/and NaOH. The slowly formed colloidal Pt nanoparticles were studied by high-resolution electron microscopy. In dilute solutions, the rate of reduction was proportional to the square of the Pt(II) concentration. In the presence of citrate and NaOH, the reduction occurs more slowly.

CuAlPd Alloys for Sensor and Actuator Applications

Z. C. LIN, W. YU, R. H. ZEE and B. A. CHIN, *Intermetallics*, 2000, 8, (5–6), 605–611

CuAlPd alloys were found to have an austenite transformation temperature range of 115–370°C, and hysteresis range from 17–85°C, depending on composition, heat treatment and working process. Optimal shape memory properties were found for Cu-13.1 wt.% Al-2.4 wt.% Pd.

The Effect of Alloying of Palladium with Silver and Rhodium on the Hydrogen Solubility, Miscibility Gap and Hysteresis

A. K. M. FAZLE KIBRIA and Y. SAKAMOTO, *Int. J. Hydrogen Energy*, 2000, 25, (9), 853–859

The variation of H solubilities in Pd-5.0 and 10.0 at.% Ag and Pd-5.0 and 10.0 at.% Rh alloys was studied by a gas phase method. An increase of low pressure H solubility with increasing Ag content and a decrease of it with increasing Rh content occurs. The plateau pressure (p_{plat}) of Pd-Rh-H had a remarkably higher value than that of Pd-Ag-H. The p_{plat} value decreased with increasing Ag content, whereas it increased with increasing Rh content. Pd-10.0 at.% Ag-H showed the lowest loss of energy for hysteresis.

Insights into the Elimination of HCHO from the Clusters [M_n(CO)_m(COOMe)]⁺ (M_n = Ru₆C, m = 16; M_n = Rh₆, m = 15) Provided by Electrospray Mass Spectrometry

P. J. DYSON, N. FEEDER, B. F. G. JOHNSON, J. S. MCINDOE and P. R. R. LANGRIDGE-SMITH, *J. Chem. Soc., Dalton Trans.*, 2000, (12), 1813–1815

The energy-dependent electrospray ionisation mass spectra of the methoxy adducts of the title hexanuclear clusters [Ru₆C(CO)₁₇] and [Rh₆(CO)₁₆] have shown that loss of HCHO takes place during the fragmentation processes. The differences in fragmentation patterns between the two clusters were correlated to their macroscopic chemical properties.

CHEMICAL COMPOUNDS

The Reactions of [M(dppe)₂] (M = Pd, Pt) with Elemental Selenium or Tellurium: Preparation and Structure of the Platinum Polyselenide [PtSe₄(dppe)]

M. R. LEWTAS, C. P. MORLEY and M. DI VAIRA, *Polyhedron*, 2000, 19, (7), 751–756

Reaction of [Pt(dppe)₂] (1) (dppe = 1,2-bis(diphenylphosphino)ethane) with Se, or of [PtCl₂(dppe)] with Li polyselenide, gave [PtSe₄(dppe)]. Reaction of (1) with Te, followed by treatment with CH₂Cl₂, gave [Pt₃(μ₃-Te)₂(dppe)₃]Cl₂. [Pd(dppe)₂] reacts with Se to give [Pd₂(μ-Se)₂(dppe)₂] or [Pd₃(μ₃-Se)₂(dppe)₃]Cl₂, depending upon the conditions.

Synthesis and Utility of Novel C-meso-Glycosylated Metalloporphyrins

M. CORNIA, M. MENOZZI, E. RAGG, S. MAZZINI, A. SCARAFONI, F. ZANARDI and G. CASIRAGHI, *Tetrahedron*, 2000, 56, (24), 3977–3983

C-meso-glycosylated porphyrins were prepared by using either a dipyrromethane/aldehyde [2+2] cyclocondensation protocol, or a direct pyrrole/aldehyde macrocyclisation. When complexed with Pd(II), and fully liberated from the protecting groups, bis-uridiny porphyrin and tetra-glycosylated porphyrin gave H₂O-soluble metallated species (1). (1) are efficient DNA cleavers with visible light at room temperature.

γ-Halogenated Iridium(III) Acetylacetonates

V. G. ISAKOVA, I. A. BAIDINA, N. B. MOROZOVA and I. K. IGUMENOV, *Polyhedron*, 2000, 19, (9), 1097–1103

Ir(acacX)_n(acac)_{3-n} (acacX = CH₃COCXCOCH₃, acac = CH₃COCHCOCH₃; n = 1, 2, 3; X = F, Cl, Br, I) were prepared and purified. DTA and TGA studies showed the monosubstituted complexes to be the most volatile and disubstituted complexes to be less volatile. The volatility of γ-halogenated Ir(III) acetylacetonates is increased in comparison with the initial Ir(III) tris-acetylacetonate.

Structure and Magnetism in Pr₃RuO₇

F. WISS, N. P. RAJU, A. S. WILLS and J. E. GREEDAN, *Int. J. Inorg. Mater.*, 2000, 2, (1), 53–59

The ordered fluorite, Pr₃RuO₇, (1) was synthesised for the first time and its crystal structure was assigned as Cmc₂m. Relatively well separated zig-zig chains of corner-sharing RuO₆ octahedra were present. Magnetic susceptibility data of (1) show a Curie-Weiss behaviour for T > 225 K with C = 5.96(4) emu K mol⁻¹ and θ_c = +11(2) K. From the paramagnetic regime, an effective magnetic moment was assigned to Ru(5+) which is slightly reduced from the spin-only value, suggesting localised electrons at this site.

PHOTOCONVERSION

Multiple Ligand-Based Emissions from a Platinum(II) Terpyridine Complex Attached to Pyrene

J. F. MICHALEC, S. A. BEJUNE and D. R. McMILLIN, *Inorg. Chem.*, 2000, 39, (13), 2708–2709

Attachment of an electron-rich aryl substituent at the 4' position of 2,2':6',2''-terpyridine (trpy) in Pt(trpy)Cl⁺ endows the low-lying excited state with intraligand charge-transfer character (ILCT), enhances the emission intensity, extends the excited-state lifetime and inhibits exciplex quenching by Lewis bases. When pyrene is the substituent, the ILCT character of the absorption becomes dominant and the lifetime extends to 64 μ s.

Photophysical and Photoelectrochemical Properties of the Bis(2,2'-bipyridine)(4,4'-dimethylthio-2,2'-bipyridine)ruthenium(II) Complex

H. E. TOMA, R. M. SERRASQUEIRO, R. C. ROCHA, G. J. F. DEMETS, H. WINNISCHOFER, K. ARAKI, P. E. A. RIBEIRO and C. L. DONNICI, *J. Photochem. Photobiol. A: Chem.*, 2000, 135, (2–3), 185–191

[Ru(bipy)₂(Sbipy)]²⁺ (Sbipy = 4,4'-dimethylthio-2,2'-bipyridine) (1) exhibits strong charge-transfer bands at 450 nm and luminescence emission at 630 nm ($\tau_{1/2}$ = 0.91 μ s). The thioether groups of Sbipy were used as strong binding sites for pentacyanoferrate ions, allowing immobilisation of (1) into Ni Prussian-blue type films. These display photoaction response to visible light in the presence of dissolved O₂.

ELECTRODEPOSITION AND SURFACE COATINGS

Electrodeposition of Platinum from an Alkaline Electrolyte

S. S. DJOKIĆ, *Plat. Surf. Finish.*, 2000, 87, (5), 145–147

Electrodeposition of Pt from an alkaline electrolyte at 65°C gave smooth Pt coatings with cauliflower surface morphology. Uniform, crack-free coatings of Pt were obtained when the thickness was < 5 μ m. Based on XRD, the electrodeposited Pt films were polycrystalline with crystallite size from 6–15 nm.

Preparation and Characterization of Platinum Black Electrodes

B. ILIC, D. CZAPLEWSKI, P. NEUZIL, T. STANCZYK, J. BLOUGH and G. J. MACLAY, *J. Mater. Sci.*, 2000, 35, (14), 3447–3457

Deposition time and cure temperature were found to influence the quality and morphology of electrochemically deposited Pt black layers on evaporated Pt electrodes. When the Pt black deposition time is < 60 seconds, large voids were clearly seen throughout the electrode due to possible passivating contaminants. Non-uniform outgrowth of Pt black was observed for deposition current densities > 100 mA cm⁻². The reproducibility of highly adherent platinumised electrodes was achieved.

Chemical Fluid Deposition: A Hybrid Technique for Low-Temperature Metallization

D. P. LONG, J. M. BLACKBURN and J. J. WATKINS, *Adv. Mater.*, 2000, 12, (12), 913–915

High-purity films of Pt, Pd, Au and Rh have been deposited onto inorganic and polymer substrates by chemical reduction of organometallics in sc-CO₂ using the chemical fluid deposition technique. A 180 nm thick Rh film (1) was deposited onto Pd-seeded polyimide using [acac(Rh)(COD)] in sc-CO₂ and a forty-fold molar excess of H₂ at 60°C and 165 bar. (1) is polycrystalline and free of C contamination.

Surface Activation of Polyimide with Dielectric Barrier Discharge for Electroless Metal Deposition

H. ESROM, R. SEEBÖCK, M. CHARBONNIER and M. ROMAND, *Surf. Coat. Technol.*, 2000, 125, (1–3), 19–24

A novel activation process (1) for the electroless plating of non-conductive materials using a dielectric barrier discharge (DBD) is reported. (1) is based on the plasma-induced chemical reduction at atmospheric pressure in air of Pd acetate layers resulting in the formation of Pd on non-active surfaces. Fast surface activation of polymers such as polyimide (2) occurs in only a few seconds using a simple DBD device. The DBD-induced Pd layers on (2) exhibit high activity with regard to initiation of electroless Cu plating.

APPARATUS AND TECHNIQUE

Highly Sensitive MISFET Sensors with Porous Pt-SnO₂ Gate Electrode for CO Gas Sensing Applications

H. FUKUDA, K. KASAMA and S. NOMURA, *Sens. Actuators B, Chem.*, 2000, 64, (1–3), 163–168

A new porous Pt-SnO₂-gate MISFET gas sensor (1) has been demonstrated for the detection of small amounts of CO. (1) combines the catalytic properties of Pt, and the spillover effect onto SnO₂, with surface-sensitive MISFETs. Using (1), it was possible to detect 54 ppm of CO with a response time < 1 min at 27°C. The good response indicates that (1) can be used at a much lower temperature (27–100°C) than can conventional solid-state gas sensors.

Palladium-Modified Yttria-Stabilized Zirconia Membranes

J. KIM and Y. S. LIN, *Ind. Eng. Chem. Res.*, 2000, 39, (6), 2124–2126

Thin porous yttria-stabilised zirconia (YSZ) membranes (1) were modified with Pd by the reservoir method. Multiple Pd impregnations inside (1) resulted in a pore reduction and an increase in Pd concentration. He permeation experiments showed that the average permeability decreased from 3.13 × 10⁻⁵ to 7.34 × 10⁻⁶ mol/(m² s Pa) after four Pd impregnations. XRD indicated that the prepared (1) had pure YSZ and Pd phases. The Pd phase became continuous after four impregnations, which was confirmed by electrical conductivity measurements.

Iridium-Based Electrocatalytic Systems for the Determination of Insulin

M. PIKULSKI and W. GORSKI, *Anal. Chem.*, 2000, 72, (13), 2696–2702

A homogeneous electrochemical catalytic system for the determination of insulin is based on the oxidation of insulin by Cl complexes of Ir(IV) (1). The rate constants are equal to 25, 900 and 8400 l mol⁻¹ s⁻¹ for the oxidation of insulin by IrCl₆²⁻, Ir(H₂O)Cl₅⁻ and Ir(H₂O)₂Cl₄, respectively. Electroplating of aquated (1) on glassy C electrode gave an IrO₂ surface film, which was used in a heterogeneous detection system for insulin.

Amperometric On-Line Sensor for Continuous Measurement of Hypoxanthine Based on Osmium-Polyvinylpyridine Gel Polymer and Xanthine Oxidase Bionzyme Modified Glassy Carbon Electrode

L. MAO and K. YAMAMOTO, *Anal. Chim. Acta*, 2000, 415, (1–2), 143–150

An amperometric biosensor using Os-polyvinylpyridine gel polymer (Os-gel-horseradish peroxidase (HRP)) and xanthine oxidase (XOD) bionzyme has been developed for use in a thin-layer radial flow cell for on-line measurement of hypoxanthine (1). In continuous-flow amperometric experiments, Os-gel-HRP/XOD/glassy coated electrodes show linear and sensitive responses towards (1) for concentrations of 0.5–80 μM with a detection limit of 0.2 μM.

HETEROGENEOUS CATALYSIS

Highly Selective and Stable Multimetallic Catalysts for Propane Dehydrogenation

S. R. DE MIGUEL, E. L. JABLONSKI, A. A. CASTRO and O. A. SCENZA, *J. Chem. Technol. Biotechnol.*, 2000, 75, (7), 596–600

Mono- (Pt), bi- (Pt-Sn, Pt-Pb, Pt-Ga) and trimetallic (Pt-Sn-Ga) catalysts based on Pt and supported on Al₂O₃, Al₂O₃ doped with K, and ZnAl₂O₄ were tested in propane dehydrogenation (both in continuous and in pulse reactors) under severe process conditions. Pt-Sn-Ga/ZnAl₂O₄ had a better and more stable performance (high yield to propene and low coke deposition), than the other bi- and trimetallic systems and a commercial catalyst.

Poly(N-isopropylacrylamide)-Grafted Silica as a Support of Platinum Colloids: Preparation Method, Characterization, and Catalytic Properties in Hydrogenation

K. SUZUKI, T. YUMURA, M. MIZUGUCHI, Y. TANAKA, C.-W. CHEN and M. AKASHI, *J. Appl. Polymer Sci.*, 2000, 77, (12), 2678–2684

Well-dispersed Pt colloids were synthesised *in situ* on the surface of poly(N-isopropylacrylamide)-grafted silica via the reduction of PtCl₆²⁻ by C₂H₅OH. The immobilised Pt colloids were active and stable heterogeneous catalysts (1) for hydrogenation of allyl alcohol in C₂H₅OH. (1) are recyclable after centrifugation.

Methyldecalin Hydrocracking over Palladium/Zeolite-X

S. SAYAN, B. DEMIREL and J. PAUL, *Fuel*, 2000, 79, (11), 1395–1404

Studies of hydrocracking of methyldecalin over Pd/rare earth exchange X-type zeolite showed that an increase in temperature from 325 to 350°C resulted in a shift from the preferred cracking products to aromatics, an enhanced amount of light hydrocarbon off-gases, and a higher coverage of C residues (and a lower coverage of reactant molecules). Pd is the agent for H₂ dissociation and repopulation of acid sites.

Catalytic Dehydrogenation of Hydrocarbons in Palladium Composite Membrane Reactors

P. QUICKER, V. HÖLLEIN and R. DITTMAYER, *Catal. Today*, 2000, 56, (1–3), 21–34

Electroless Pd plating was confirmed to be a suitable method for coating ceramic supports. Composite Pd-steel membranes could be prepared by high velocity oxy-fuel spraying and a combined method of electroplating and electroless plating. Coated membranes were employed for H₂ separation in lab-scale membrane reactors during the dehydrogenation of ethylbenzene to styrene and propane to propylene. The removal of H₂ significantly increased the olefin yield, compared to the corresponding conventional packed-bed reactor results.

Palladium Catalysts on Activated Carbon Supports Influence of Reduction Temperature, Origin of the Support and Pretreatments of the Carbon Surface

M. GURRATH, T. KURETZKY, H. P. BOEHM, L. B. OKHLOPKOVA, A. S. LISITSYN and V. A. LIKHOLOBOV, *Carbon*, 2000, 38, (8), 1241–1255

Activated carbons produced from peat, coconut shell and by pyrolysis of hydrocarbons were treated with O₂, Cl₂, H₂ or NH₃ at elevated temperatures. Pd was deposited from anionic (H₂PdCl₄), neutral (Pd(OAc)₂ in acetone) and cationic ([Pd(NH₃)₄](NO₃)₂) complexes. Temperature-programmed reduction, CO chemisorption and the olefin hydrogenation reaction were used to investigate the possible effects of preparation variables. The origin of the C support and the temperature of the catalyst reduction with H₂ had most influence on the properties of the catalysts.

Polymer-Supported Ruthenium Porphyrins: Versatile and Robust Epoxidation Catalysts with Unusual Selectivity

X.-Q. YU, J.-S. HUANG, W.-Y. YU and C.-M. CHE, *J. Am. Chem. Soc.*, 2000, 122, (22), 5337–5342

Carbonyl Ru(II) 5,10,15-tris(4-R-phenyl)-20-(4-hydroxyphenyl)porphyrins (R = Cl, Me) covalently bonded to Merrifield's peptide resin were prepared. These new heterogenised metalloporphyrin epoxidation catalysts (1) exhibit a high versatility and stability. (1) with R = Cl catalyse Cl₂pyNO epoxidation of alkenes such as aromatic and aliphatic terminal alkenes and α,β-unsaturated ketones. (1) are reusable.

Microwave-Assisted Rapid Incorporation of Ruthenium into Lacunary Keggin-Type Polyoxotungstates: One-Step Synthesis, ⁹⁹Ru, ¹⁸³W NMR Characterization and Catalytic Activity of [PW₁₁O₃₉Ru^{IV}(DMSO)]⁵⁻

A. BAGNO, M. BONCHIO, A. SARTOREL and G. SCORRANO, *Eur. J. Inorg. Chem.*, 2000, (1), 17–20

[RuCl₂(DMSO)₄] was shown to react with the lacunary tungstate ligand [PW₁₁O₃₉]⁷⁻ in H₂O at 200°C under microwave irradiation, leading to the complete incorporation of a Ru atom into the polyoxometallate framework, and to the selective formation of the diamagnetic, air-stable [PW₁₁O₃₉Ru^{II}(DMSO)]⁵⁻ (1). (1) exhibited remarkable catalytic activity in the presence of NaIO₄ or KHSO₅ in the oxidation of cyclooctene and adamantane, respectively.

HOMOGENEOUS CATALYSIS

Palladium-Catalyzed Carbonylation of Aryl Halides – A Detailed Investigation of the Alkoxy-carbonylation of 4-Bromoacetophenone

W. MÄGERLEIN, M. BELLER and A. F. INDOLESE, *J. Mol. Catal. A: Chem.*, 2000, 156, (1–2), 213–221

The homogeneous Pd-catalysed alkoxy-carbonylation of 4-bromoacetophenone with *n*-butanol to give the corresponding benzoic acid ester (1) was investigated. The highest catalyst efficiency was observed at 130°C and low CO pressures using neat *n*-butanol as the solvent, NEt₃ as the base and Pd(PPh₃)₄ or PdCl₂(PhCN)₂/PPh₃ as the catalyst precursor. A strong dependence of the catalyst activity and stability on the phosphine concentration was found. Catalyst productivities (turnover number) of up to 7000 (70% yield of (1)) were achieved.

Microwave-Assisted, Solventless Suzuki Coupling Reactions on Palladium-Doped Alumina

G. W. KABALKA, R. M. PAGNI, L. WANG, V. NAMBOODIRI and C. M. HAIR, *Green Chem.*, 2000, 2, (3), 120–122

5% Pd/KF/Al₂O₃ (1) has been used as the catalyst for solventless microwave-assisted Suzuki reactions of aryl halides with boronic acids and vinyl boronic acids. (1) can be readily recycled via simple filtration. Other benefits include straightforward recovery of product, potential simple commercial scale up and low waste protocols due to the absence of solvents.

A Convenient Synthesis of Heteroaryl Benzoic Acids via Suzuki Reaction

Y. GONG and H. W. PAULS, *Synlett*, 2000, (6), 829–831

The Suzuki reaction was applied as a general one-step method for heteroaryl benzoic acid synthesis from heteroaryl halides and carboxybenzene boronic acids. The coupling is carried out in the presence of Pd(PPh₃)₄ (1) and Na₂CO₃ in 50% aqueous acetonitrile. A high yield was maintained when (1) was substituted by Pd(PPh₃)₂Cl₂ and Pd(OAc)₂/P(*o*-tolyl)₃, although prolonged reaction times were required.

Rhodium(I)-Catalyzed Addition of Phenols to Dienes. A New Convergent Synthesis of Vitamin E

H. BIENAYMÉ, J.-E. ANCEL, P. MEILLAND and J.-P. SIMONATO, *Tetrahedron Lett.*, 2000, 41, (18), 3339–3343

A catalytic amount of [RhCl(COD)₂], diphenylphosphinobutane and K₂CO₃ in toluene resulted in the regioselective arylation of β-springene with trimethylhydroquinone under mild conditions. Further steps resulted in synthesis of vitamin E with an overall 50% yield. Other phenolic compounds and 2-substituted-1,3-dienes were also shown to undergo this transformation.

Hydroformylation Reactions in Supercritical

Carbon Dioxide Using Insoluble Metal Complexes

M. F. SELLIN and D. J. COLE-HAMILTON, *J. Chem. Soc., Dalton Trans.*, 2000, (11), 1681–1683

Rh phosphite catalysts (1) prepared *in situ* from [Rh₂(OAc)₄] and P(OPh)₃, P(OC₆H₄-4-C₆H₁₉)₃ or Ph₂PCH₂CH(CO₂C₁₆H₃₃)CH₂CO₂C₁₆H₃₃, which are insoluble in sc-CO₂, show high activity and excellent linear selectivity in the hydroformylation of hex-1-ene. (1) can be recycled by flushing the products from the reactor using sc-CO₂ at the reaction temperature and pressure with no Rh leaching.

A 14-Electron Ruthenium Hydride: the Key Intermediate in the Synthesis of Ruthenium Carbene Complexes; X-ray Structure of [RuHCl(PPR^t)₂]

P. A. VAN DER SCHAAF, R. KOLLY and A. HAFNER, *Chem. Commun.*, 2000, (12), 1045–1046

A simple one-pot procedure for the synthesis of Ru benzyldienes (Grubbs' catalyst) (1) has been developed, in which the key intermediate, a novel 14-electron Ru monohydride, [RuHCl(PPR^t)₂] (2), is prepared from [RuCl₂(cod)], 2 equivalents of PPR^t, and NEt₃ in boiling propan-2-ol without the use of H₂ gas. (2) was reacted with HCl, an alkyne and styrene to give (1).

FUEL CELLS

A Study of Methanol Electro-Oxidation Reactions in Carbon Membrane Electrodes and Structural Properties of Pt Alloy Electro-Catalysts by EXAFS

T. PAGE, R. JOHNSON, J. HORMES, S. NODING and B. RAMBABU, *J. Electroanal. Chem.*, 2000, 485, (1), 34–41

Transition metal alloy electrocatalysts (Pt-Fe/C, Pt-Co/C, Pt-Ni/C, Pt-Cu/C) were evaluated as potential alternatives to direct oxidation of DMFCs and compared with Pt group metal and alloy catalysts using CV and X-ray absorption spectroscopy. Pt-Co/C was found to be a better catalyst than the other transition metal alloys. Pt/C/Nafion showed the highest resistance (10⁶ Ω cm⁻²) compared with Pt-Ru/C (280 mΩ cm⁻²). The unfavourable electrochemical performance of Pt-Ru can be correlated with the observed variations in geometric structural information obtained from EXAFS and XANES.