

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Optical and Mechanical Consequences of Microstructural Alteration of Alpha Platinum Dioxide Films

L. MAYA, L. M. ANOVITZ, T. THUNDAT and C. S. YUST, *J. Vac. Sci. Technol. A*, 1999, 17, (3), 1036–1039

The microstructure of α -PtO₂ (1) films prepared by d.c.-sputtering consisted of a porous random assembly of platelets. Under very light mechanical pressure, microstructural altering of crystalline (1) occurred causing a flattening of platelets visible under reflected light of the affected areas.

Reactions of Laser-Ablated Platinum and Palladium Atoms with Dioxygen. Matrix Infrared Spectra and Density Functional Calculations of Platinum Oxides and Complexes and Palladium Complexes

W. D. BARE, A. CITRA, G. V. CHERTIHIN and L. ANDREWS, *J. Phys. Chem. A*, 1999, 103, (28), 5456–5462

Pt and Pd atoms produced by laser ablation were reacted with O₂ diluted in Ar during condensation at 10 K. The reaction products, including the M(O₂) and (O₂)M(O₂) complexes prepared with thermal metal atoms, and the Pt oxides PtO, OPtO, PtO₂, OOPtO and (O₂)PtO, were analysed by matrix IR spectroscopy. Density functional theory calculations were made on the product molecules.

Chiral Magnetic Domain Structures in Ultrathin FePd Films

H. A. DÜRR, E. DUDZIK, S. S. DHESI, J. B. GOEDKOOP, G. VAN DER LAAN, M. BELAKHOVSKY, C. MOCUTA, A. MARTY and Y. SAMSON, *Science*, 1999, 284, (5423), 2166–2168

Ultrathin FePd films were investigated by circular dichroism in X-ray resonant magnetic scattering. For single crystalline FePd alloy layers grown by molecular beam epitaxy onto a MgO(001) substrate, magnetic flux closure domains were found whose thickness constituted a large fraction (~25%) of the total film.

Transient Experiments on CO₂ Formation by the CO Oxidation Reaction over Oxygen-Rich Ru(0001) Surfaces

A. BÖTTCHER, M. ROGOZIA, H. NIEHUS, H. OVER and G. ERTL, *J. Phys. Chem. B*, 1999, 103, (30), 6267–6271

Using a molecular beam technique, transient CO titration experiments of oxygen-rich Ru(0001) surfaces at 300–700 K revealed 2 distinct reaction channels in the transient CO₂ formation rate. The first reaction channel is related to the recombination of CO with O atoms already located on the surface. The second reaction, which was observed at > 400 K, is controlled by the diffusion of O atoms from the near-surface region towards the surface.

CHEMICAL COMPOUNDS

One-Phase Synthesis of Thiol-Functionalized Platinum Nanoparticles

C. YEE, M. SCOTTI, A. ULMAN, H. WHITE, M. RAFAILOVICH and J. SOKOLOV, *Langmuir*, 1999, 15, (13), 4314–4316

Using THF and LiB(C₂H₅)₃H (“superhydride”), Pt nanoparticles functionalised by octadecanethiol were obtained. XRD, TEM and FTIR showed that the nanoparticles are single crystals with f.c.c. structure and average size is ~ 3 nm. The octadecyl chains close packed in a solid-like assembly.

A Cationic Tetranuclear Platina- β -diketonate Complex of a Platina- β -diketone – An Organometallic Analogue of Platinum Blue Complexes

M. GERISCH, C. BRUHN and D. STEINBORN, *Polyhedron*, 1999, 18, (14), 1953–1956

The platina β -diketone [Pt₂{(COMe)₂H}₂(μ -Cl)₂] reacted with 2,2'-bipyridine (bpy) in the presence of TlPF₆ to give the title cationic complex [(bpy)Pt(μ -COMe)₂Pt[(COMe)₂H]₂][PF₆]₂ (1). X-ray structure analysis established that in the solid state the complex (1)·2CH₂Cl₂ consists of tetranuclear dications with Pt, zigzag chains (Pt–Pt–Pt angle: 124.71(3)°). The Pt···Pt distances (3.094(1), 3.183(1) Å) indicated closed shell d⁸–d⁸ interactions.

Interaction of Platinum Fulleride C₆₀Pt with Deuterium

N. F. GOLDSHLEGER, B. P. TARASOV, YU. M. SHUL'GA, O. S. ROSCHUPKINA, A. A. PEROV and A. P. MORAVSKII, *Izv. RAN, Ser. Khim.*, 1999, (5), 999–1002

The X-ray photoelectron spectra and catalytic properties of platinum fulleride (C₆₀Pt) were investigated. The value of bond energy Pt4f_{7/2} (72.4 eV) found for Pt in C₆₀Pt was attributed to the partial charge transfer from Pt to C₆₀. The interaction of solid C₆₀Pt with gaseous deuterium (D) leads to the formation of fullerene deuterides C₆₀D_x and Pt clusters.

Correlation between Structural and Solution Calorimetric Data for Cp*Ru(PR₃)₂Cl (Cp* = C₅Me₅) Complexes

D. C. SMITH, C. M. HAAR, L. LUO, C. LI, M. E. CUCULLU, C. H. MAHLER, S. P. NOLAN, W. J. MARSHALL, N. L. JONES and P. J. FAGAN, *Organometallics*, 1999, 18, (12), 2357–2361

Single crystal XRD data on Cp*Ru(L)₂Cl (L = PMe₃, PPhMe₂, PMePh₂, PPh₃, PEt₃, AsEt₃, PⁿBu₃) and Cp*Ru(dmpm)Cl were correlated with enthalpies of ligand substitution previously determined from solution calorimetry. The cone angle of the phosphine ligand and the Ru–P bond distance were found to be proportional to the enthalpy of reaction.

ELECTROCHEMISTRY

Electrocatalytic Oxidation of NADH at Graphite Electrodes Modified with Osmium Phenanthroline-dione

I. C. POPESCU, E. DOMÍNGUEZ, A. NARVÁEZ, V. PAVLOV and I. KATAKIS, *J. Electroanal. Chem.*, 1999, **464**, (2), 208–214

Os(4,4'-dimethyl-2,2'-bipyridine)₂(1,10-phenanthroline 5,6-dione), adsorbed on spectrographic graphite, oxidises NADH reversibly. CV measurements confirmed that the phenidone ligand redox process involves 2 electrons and 2 protons. The rate constant for the electrocatalytic oxidation of NADH (at pH 6.1, $k_{1,[NADH]=0} = 1.9 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$) as well as its pH dependence (pH 5.5–8.1) were evaluated.

A Neutron Reflectivity Study of [Os(bipy)₂(PVP)₁₀Cl]⁺ Polymer Film Modified Electrodes: Effect of Redox State and Counter Ion

R. W. WILSON, R. CUBITT, A. GLIDLE, A. R. HILLMAN, P. M. SAVILLE and J. G. VOS, *Electrochim. Acta*, 1999, **44**, (20), 3533–3548

[Os(bipy)₂(PVP)₁₀Cl]⁺ polymer films were studied using neutron reflectivity. The effect of redox cycling of the films in electrolyte was dependent upon the counter ion: using *p*-TSA increased solvent content with little change in film thickness, whilst perchlorate caused a decrease in both of these parameters. Holding the films in Os(II) and Os(III) oxidation states had less effect than changing the counter ion.

PHOTOCONVERSION

Control of the Photochemistry of Ru₃(CO)₁₂ and Os₃(CO)₁₂ by Variation of the Solvent

N. E. LEADBEATER, *J. Organomet. Chem.*, 1999, **573**, (1–2), 211–216

The photosubstitution of CO in M₃(CO)₁₂ (M = Ru, Os) was examined in diethyl ether, ethyl acetate and acetonitrile media. UV photolysis of M₃(CO)₁₂ with PPh₃ led to M₃(CO)_{12-n}(PPh₃)_n (n = 1–3). Photolysis of M₃(CO)₁₂ with RSH (R = Et, Ph) gave HM₃(μ-SR)(CO)₁₀ which on prolonged photolysis generated M₃(μ-S)(CO)₁₀. Photolysis of C₂H₅-saturated diethyl ether or ethyl acetate solutions of M₃(CO)₁₂ led to no net photoreaction with Ru, whereas for Os, Os(CO)₄(η²-C₂H₄) was formed.

New Luminescent Ruthenium Complexes with Extended π Systems

G. ALBANO, P. BELSER, L. DE COLA and M. T. GANDOLFI, *Chem. Commun.*, 1999, (13), 1171–1172

Polypyridyl Ru(II) complexes (1) have been synthesised from naphtho[2,3-*f*][1,ω]phenanthroline-9,14-dicarbonitrile and naphtho[2,3-*f*][1,ω]phenanthroline ligands, structurally similar to dipyrrodo[3,2-*a*:2,3-*c*]phenazine. Luminescence is related to amounts of DNA, thus (1) have potential as luminescent sensors, fluorescent labels and DNA photoprobes.

ELECTRODEPOSITION AND SURFACE COATINGS

Surface-Enhanced Infrared Absorption of CO on Platinized Platinum

A. E. BJERKE, P. R. GRIFFITHS and W. THEISS, *Anal. Chem.*, 1999, **71**, (10), 1967–1974

The first observation of surface-enhanced IR spectroscopy on platinised Pt surfaces is reported. Smooth Pt electrodes were electrochemically platinised to produce regular metal island surfaces which enhanced absorption of the IR spectrum of adsorbed CO by up to 20 times. As the amount of platinisation increased, the CO band became asymmetrical, then bipolar, and finally appeared as a reflection maximum.

Characterization of Platinum-Ruthenium Electrodeposits Using XRD, AES and XPS Analysis

C. CATTANEO, M. I. SANCHEZ DE PINTO, H. MISHIMA, B. A. LÓPEZ DE MISHIMA, D. LESCANO and L. CORNAGLIA, *J. Electroanal. Chem.*, 1999, **461**, (1–2), 32–39

Pt-Ru was electrodeposited on Au substrate from Pt and Ru salts solutions. XRD showed that the electrodeposits are f.c.c. alloys and can be formed in such a way that the crystalline grains have an orientation randomly distributed or are oriented to give a crystallographic texture, perpendicular to the substrate surface. XPS revealed that there are no compounds with oxidation states different from Ru(0) and Pt(0).

Contactless Electrodeposition of Palladium Catalysts

J.-C. BRADLEY and Z. MA, *Angew. Chem. Int. Ed.*, 1999, **38**, (11), 1663–1666

Site-selective electrodeposition of catalytically active Pd on conducting graphite support particles (1–2 μm) has been achieved by polarisation with an electric field in a matrix of toluene:acetonitrile (1:1) in the presence of Pd salt solutions. The properties of these catalytic systems were controlled by modulating the electric field parameters during their preparation.

APPARATUS AND TECHNIQUE

High Temperature Pt Schottky Diode Gas Sensors on *n*-Type GaN

B. P. LUTHER, S. D. WOLTER and S. E. MOHNEY, *Sens. Actuators B, Chem.*, 1999, **56**, (1–2), 164–168

Pt Schottky diodes (1) on *n*-type GaN have been studied as detectors for H₂ and propane between 200 to 400°C. The *I*-*V* characteristics of the diodes indicate a response to H₂ at all temperatures studied, while propane is detected only at ≥ 300°C. The recovery of the diode characteristics after H₂ or propane exposure is aided by O₂ in the gas environment. (1) demonstrated good long term stability at 400°C showing no degradation of electrical properties after 500 h. These results indicate that (1) on *n*-type GaN may be able to operate as reliable H₂ or hydrocarbon gas sensors at temperatures ≤ 400°C.

Preparation of Platinum/Iridium Scanning Probe Microscopy Tips

A. H. SØRENSEN, U. HVID, M. W. MORTENSEN and K. A. MØRCH, *Rev. Sci. Instrum.*, 1999, **70**, (7), 3059–3060

A two-step electrochemical etching setup has been developed for the preparation of Pt/Ir microscopy tips. The first step was a coarse AC etching which stopped when the lower part of the wire dropped off. The second step was a fine etching made by a number of AC pulses, each of a certain duration and separated by a certain time interval. The etch mechanism is based on the formation of O_2 and H_2 at the Pt/Ir electrode when the potential is above the dissociation potential of H_2O (~ 1.23 V) and the storage of these products is in the outer layers of the Pt wire. This leads to "microexplosions" which detach the Pt from the wire surface and give rise to "etching".

HETEROGENEOUS CATALYSIS

Enantioselective Hydrogenation of Pyruvates over Polymer-Stabilized and Supported Platinum Nanoclusters

X. ZUO, H. LIU, D. GUO and X. YANG, *Tetrahedron*, 1999, **55**, (25), 7787–7804

The cinchonidine-modified enantioselective hydrogenation of pyruvates was studied over Pt/polyvinylpyrrolidone and Pt/ Al_2O_3 clusters. Catalysts with particle size < 2.0 nm gave $> 90\%$ enantioselectivity in favour of (*R*)-lactates. These colloids and clusters remained stable, with no loss of activity and enantioselectivity, even after 18 months in air at room temperature.

Selective Oxidative Decomposition of Ammonia in Water to Nitrogen Catalyzed by Platinum-Supported Titania

J. TAGUCHI, T. NAKATO and T. OKUHARA, *Chem. Lett. Jpn.*, 1999, (4), 277–278

Selective oxidative decomposition of NH_3 (or NH_3^+) in H_2O was accomplished with 0.5 wt.% Pt/ TiO_2 catalyst at 433 K under 8 atm of O_2 without having to alkalis the solution. NH_3 of 1000 ppm was converted to N_2 with very limited formation of undesirable byproducts such as NO_2^- or NO^- in solution, or N_2O in the gas phase.

High Selectivities to Ethylene by Partial Oxidation of Ethane

A. S. BODKE, D. A. OLSCHKI, L. D. SCHMIDT and E. RANZI, *Science*, 1999, **285**, (5428), 712–715

At least 85% selectivity to C_2H_4 at $> 70\%$ conversion was obtained by partial oxidation of C_2H_6 when large quantities of H_2 were added to the reaction mixture in the presence of a Pt-Sn catalyst at 950°C and a contact time of $\sim 10^{-1}$ seconds. The formation of undesirable CO and CO_2 fell from 20% to 5% when H_2 was added. Although a mixture of $H_2:O_2$ of 2:1 should be explosive at high temperatures, no flames or explosions occurred in the presence of C_2H_6 . This process is promising for the replacement of steam cracking in the production of C_2H_4 .

A New Route to Medium and Large Heterocyclic Compounds

T. VENTRICE, E. M. CAMPI, W. R. JACKSON and A. F. PATTI, *Chem. Commun.*, 1999, (16), 1463–1464

Hydrogenation of nitrobenzenes bearing aldehyde-containing substituents over 10% Pd/C and/or PtO₂ gave medium and/or large heterocyclic amines by simple or dimeric cyclisation in moderate to good yields. Standard conditions were 1 atm H_2 , ambient temperature, with Pd (5.6×10^{-5} g atom) for reaction on ~ 0.4 mmol scale with substrate concentration of 4.8×10^{-1} M. Larger amounts of Pt (3×10^{-4} g atom) were employed.

Sol-Gel Preparation and Thermal Stability of Pd/ γ - Al_2O_3 Catalysts

C. K. LAMBERT and R. D. GONZALEZ, *J. Mater. Sci.*, 1999, **34**, (13), 3109–3116

Highly dispersed Pd/ γ - Al_2O_3 catalysts with high surface areas and narrow pore size distributions were prepared by the sol-gel technique using boehmite (AlOOH) and various Pd compounds. The samples were calcined at 400°C in flowing O_2 to decompose the Pd complex and change the phase of the support to γ - Al_2O_3 . The amount of sintering experienced by a Pd/ γ - Al_2O_3 catalyst prepared by this method is less than that of a catalyst prepared by the traditional method of ion-exchange due to the well-defined pore structure.

HOMOGENEOUS CATALYSIS

Palladium Catalysed Pronucleophile Addition to Unactivated Carbon-Carbon Multiple Bonds

Y. YAMAMOTO and U. RADHAKRISHNAN, *Chem. Soc. Rev.*, 1999, **28**, (3), 199–207

The Pd-catalysed addition of pronucleophiles to C-C multiple bonds was investigated. The Pd-catalysed hydrocarbonation of allenes and allylation of pronucleophiles using alkynes was achieved. This methodology was also successfully applied to the hydrocarbonation of non-conjugated alkenes such as methylenecyclopropanes. Also, hydroamination reactions were utilised efficiently to obtain biologically important allylic amines and important classes of N-containing heterocycles.

Electrochemical Cleavage of Allyl Aryl Ethers and Allylation of Carbonyl Compounds: Umpolung of Allyl-Palladium Species

D. FRANCO, D. PANYELLA, M. ROCAMORA, M. GOMEZ, J. C. CLINET, G. MULLER and E. DUÑACH, *Tetrahedron Lett.*, 1999, **40**, (31), 5685–5688

The electrochemical Pd-catalysed cleavage of the C-O bond of allyl aryl ethers was shown as a new alternative for allyl ether deprotection. The allyl transfer from the allyl ether to the carbonyl group in various 2-allyloxy benzaldehydes was established and is an example of allyl-Pd reactivity umpolung (reversal of reactivity). Pd(II) complexes, associated to chelating N ligands were shown to be efficient catalyst precursors for these mild electrochemical reactions.

Comprehensive Kinetic Screening of Catalysts Using Reaction Calorimetry

D. G. BLACKMOND, T. ROSNER and A. PFALTZ, *Org. Process Res. Dev.*, 1999, 3, (4), 275–280

A protocol based on reaction calorimetry was developed that offers a multidimensional kinetic and stability profile of a catalyst candidate in liquid and multiphase reactions. The experiments helped to identify new Pd complexes with N ligands as catalysts that are efficient, relatively stable and more active than catalysts based on phosphine ligands which are usually employed in Heck coupling reactions.

Allylic Substitution with Dendritic Palladium Catalysts in a Continuously Operating Membrane Reactor

N. BRINKMANN, D. GIEBEL, G. LOHMER, M. T. REETZ and U. KRAGL, *J. Catal.*, 1999, 183, (2), 163–168

Diaminopropyl-type dendrimers (1) bearing Pd phosphine complexes were found to be retained by ultra- and nanofiltration membranes. (1) were used as catalysts for allylic substitution in a continuously operating chemical membrane reactor. Retention rates were > 99.9% resulting in a sixfold increase of the total turnover number for the Pd catalyst. (1) are useful for homogeneous catalyst recovery.

Counter-Ligand and Solvent Dependent Oxygen-Metal Interactions of Hemilabile Coordinating Hydroxy Groups in Chiral Diphosphine Rhodium(I) Hydrogenation Catalysts

S. BORNIS, R. KADYROV, D. HELLER, W. BAUMANN, J. HOLZ and A. BÖRNER, *Tetrahedron: Asymmetry*, 1999, 10, (8), 1425–1431

The interaction of the hemilabile co-ordinating HO-groups with Rh in Rh[(R,R)-1,4-bis(diphenylphosphino)butane-2,3-diol] was shown to be strongly dependent upon the nature of the counter ligand and the solvent. Due to their strong π -accepting properties, olefins were found to strengthen the attractive interaction between the HO-group and the metal. Counter ligands with reduced π -accepting properties such as MeOH do not favour these interactions. Spectroscopic and catalytic investigations demonstrated that the η^3 -co-ordination mode of the tetradentate ligand was responsible for the deceleration of the asymmetric hydrogenation.

Purification Technique for the Removal of Ruthenium from Olefin Metathesis Reaction Products

H. D. MAYNARD and R. H. GRUBBS, *Tetrahedron Lett.*, 1999, 40, (22), 4137–4140

Ring-closure metathesis products of reactions using $\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2$ as a catalyst were purified of unwanted Ru by utilising the H_2O -soluble co-ordinating phosphine, tris(hydroxymethyl)phosphine, $\text{P}(\text{CH}_2\text{OH})_3$, (1). An aqueous extraction or silica gel purification may be used. In the case of an aqueous extraction, 10 equivalents of (1) is required to transfer the Ru to the H_2O phase.

Acyclic Diene Metathesis (ADMET) Depolymerization: Ethenolysis of 1,4-Polybutadiene Using a Ruthenium Complex

M. D. WATSON and K. B. WAGENER, *J. Polym. Sci. A: Polym. Chem.*, 1999, 37, (12), 1857–1861

α,ω -Vinyl-terminated butadiene oligomers were obtained by the cross-metathesis of C_2H_4 and 1,4-polybutadiene catalysed by $\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2$. The trend in conversion with varied ethylene pressure was studied in order to obtain the highest conversion to the monomer 1,5-hexadiene.

Ruthenium-Oxo and -Tosylimido Porphyrin Complexes for Epoxidation and Aziridination of Alkenes

C.-M. CHE and W.-Y. YU, *Pure Appl. Chem.*, 1999, 71, (2), 281–288

$[\text{Ru}^{\text{VI}}(\text{Por})\text{O}_2]$ (1) were readily obtained by the oxidation of $[\text{Ru}^{\text{IV}}(\text{Por})(\text{CO})(\text{MeOH})]$ with PhIO or *m*-chloroperoxybenzoic acid. Similarly, PhINTs gave $[\text{Ru}^{\text{VI}}(\text{Por})(\text{NTs})_2]$ (2). (1) are good oxidants for alkene epoxidation with high selectivities being achieved. Procedures for catalytic epoxidation of alkenes using Ru porphyrin catalysts were also developed. (2) was shown to undergo aziridination of alkenes and amidation of alkanes in organic solvents.

FUEL CELLS

High Energy Ball-Milled Pt and Pt–Ru Catalysts for Polymer Electrolyte Fuel Cells and Their Tolerance to CO

M. C. DENIS, G. LALANDE, D. GUAY, J. P. DODELET and R. SCHULZ, *J. Appl. Electrochem.*, 1999, 29, (8), 951–960

$\text{Pt}_{0.5}\text{-Ru}_{0.5}$ was produced by high energy ball milling, but gave a low specific area material that performed poorly as anode catalysts because the nanocrystals had aggregated. Improved specific areas were obtained by milling Pt, Ru and Al in a 1:1:8 atomic ratio. After leaching Al, this composite catalyst ($\text{Pt}_{0.5}\text{-Ru}_{0.5}(\text{Al}_4)$) had a specific area of $38 \text{ m}^2 \text{ g}^{-1}$. It showed good H_2 oxidation performance and CO tolerance in PEFCs.

ELECTRICAL AND ELECTRONIC ENGINEERING

Magneto-Optical Recording on CoPtRe Alloy Films as a Novel Material

Y. TAKEDA, T. UMEZAWA, K. CHIBA, H. SHOJI and M. TAKAHASHI, *IEEE Trans. Magn.*, 1999, 35, (4), 2166–2177

Magneto-optical (MO) disks using CoPtRe films were investigated for blue laser recording. Figures of merit and Kerr values were estimated for a quadri-layer structure in a MO disk. About 15 nm of a thickness of CoPtRe was calculated to be suitable for optical properties. MO recordings were made on a CoPtRe disk at wavelengths of 530 and 830 nm, and both write and read processes behaved normally. The recording properties were almost equivalent to those for Co/Pt.