

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Short-Range Order in Ni-Pt Alloys

D. K. SAHA and K.-I. OHSHIMA, *J. Phys. Condens. Matter*, 1995, 7, (17), 3203–3209

The existence and shape of the diffuse intensity in $\text{Ni}_{1-x}\text{Pt}_x$ alloys with $x = 0.25, 0.35, 0.44$ and 0.50 were studied. The dependence on composition of the diffuse intensity was observed where the shape of diffuse intensity changed with Pt content, and was similar to that for Cu-Au alloy. The change in shape from disc-like for the 100 position for the $x = 0.25$ to spherical for $x = 0.5$ can be explained using a linearised correlation function.

Hydrogen Pressure-Hydrogen Content and Electrical Resistance-Hydrogen Content Relationships of Palladium and Palladium Alloy-Hydrogen Systems

F. A. LEWIS, K. KANDASAMY, R.-A. MCNICHOLL and X. Q. TONG, *Int. J. Hydrogen Energy*, 1995, 20, (5), 369–372
A technique for obtaining p - $c(n)$ - T relationships at near 25°C involving derivations from electrode potential measurements in the Pd-Pt-H system, where sensitive changes of electrical resistance can be measured, was used to examine hysteretic differences between forms of relationships in the Pd alloy-H system. Size of alloying element is a guide to change of form in p - n .

Kinetics of Hydrogen Desorption from Palladium and Ruthenium-Palladium Foils

A. L. CABRERA, E. MORALES and J. N. ARMOR, *J. Mater. Res.*, 1995, 10, (3), 779–785

Studies of absorption of H and CO at room temperature by Pd and 5% Ru-Pd foils showed that H readily diffused into the Pd and desorbed as one broad peak at ~650 K. The 5% Ru-Pd is less effective than pure Pd for the absorption and transport of H but can withstand more H absorption-desorption cycles. Activation energies for bulk diffusion obtained from H uptake measurements corresponded to 4.4 and 4.9 kcal/mol for Pd foil and Ru-Pd alloy, respectively.

Microstructural Development, Electrical Properties and Oxygen Permeation of Zirconia-Palladium Composites

C. S. CHEN, B. A. BOUKAMP, H. J. M. BOUWMEESTER, G. Z. CAO, H. KRUIDHOF, A. J. A. WINNUST and A. J. BURGGRAAF, *Solid State Ionics*, 1995, 76, (1, 2), 23–28
Studies of Y_2O_3 -stabilised cubic ZrO_2 (YSZ)-Pd dual phase composites showed a larger O permeability in the percolative composite containing 40 vol.% Pd (ZYPd40) than that of the non-percolative composite containing 30 vol.% Pd (ZYPd30). It is concluded that the transport of the O ions through the YSZ phase in the percolative system is the rate limiting step.

Characterization of Silver-Palladium Submicronic Powders. Part 1. Morphology and Thermal Properties

E. DELARUE, M. MOSTAFAVI, M. O. DELCOURT and D. REGNAULT, *J. Mater. Sci.*, 1995, 30, (3), 628–632
Submicronic Ag-Pd powders containing 70:30 and 75:25 wt.% Ag: Pd, prepared by precipitation in aqueous solution, were studied for use in the multilayer ceramic capacitor industry. The powders consisted of submicron spherically shaped particles with a narrow size distribution and very little agglomeration. They were made into a paste by blending with an organic binder, screen printed, fired and sintered into a conductive layer of resistivity, 15–30 μWcm for 2 μm thickness, with only a few remaining voids. Thermal measurements showed that alloying was achieved below 960°C.

Hydrogen-Induced Ordering in a $\text{Pd}_{0.81}\text{Au}_{0.19}$ Alloy

S.-M. LEE, T. B. FLANAGAN and G.-H. KIM, *Scr. Metall. Mater.*, 1995, 32, (6), 827–832

Ordering in $\text{Pd}_{0.81}\text{Au}_{0.19}$ alloy proceeded under the effect of large amounts of dissolved H_2 , which stabilised the ordered structure as the alloy reverted to the disordered state upon annealing in vacuo, at the same temperature used for ordering the alloy by H_2 heat treatment. The present results showed that the alloy does not order because it is not thermodynamically stable in the absence of H_2 .

Magnetization and FMR Linewidth in Annealed Co-Pd-Si Amorphous Alloys

S. MACKOVÁ, *IEEE Trans. Magn.*, 1995, 31, (2), 927–929

The effect of the annealing on the magnetic polarisation and FMR linewidth of the amorphous alloys $\text{Co}_{10}\text{Pd}_{70}\text{Si}_{20}$ and $\text{Co}_{13}\text{Pd}_{67}\text{Si}_{20}$ was studied at room temperature. A small maximum polarisation was observed at the annealing temperature of ~400°C, which corresponds to the crystallisation region. A comparison between the saturation magnetic polarisation and the effective value obtained from FMR showed that the maximum volume of Co clusters occurs for materials annealed at ~700–800°C. The possible contribution of magnetic inhomogeneities to the linewidth is discussed.

New Heavy-Electron System $\text{Ce}_3\text{Pd}_{20}\text{Si}_6$

N. TAKEDA, J. KITAGAWA and M. ISHIKAWA, *J. Phys. Soc. Jpn.*, 1995, 64, (2), 387–390

Studies of magnetic and transport properties of $\text{Ce}_3\text{Pd}_{20}\text{Si}_6$ showed that this compound is a Kondo material with a strongly enhanced C/T value of 24 J/mole K^2 at 0.2 K. This suggests that $\text{Ce}_3\text{Pd}_{20}\text{Si}_6$ is one of the heaviest-electron systems.

$\text{Cr}_{1-x}\text{Ir}_x\text{O}_2$ ($0 < x < 0.3$), a Ferromagnetic Material with High Coercivity

G. DEMAZEAU, J. P. SANCHEZ, J. H. CHOY, S. F. MATAR, V. EYERT, J. KÜBLER and F. OKINO, *J. Magn. & Magn. Mater.*, 1995, **140-144**, 165-166

Mössbauer studies of magnetic properties of the ferromagnetic lattice CrO_2 doped with Ir(IV), which has a high value for the spin-orbit coupling constant, showed that Ir(IV) in CrO_2 is mainly stabilised in such a lattice. However, after very high O₂ pressure treatment, Ir(V) was found close to the surface. The orbital contribution to the spin only magnetic moment is 8 times larger for Ir than for Cr.

Electrical and Optical Properties of Ruthenium-Related Defects in Silicon

H. PETTERSSON, H. G. GRIMMEISS, K. SCHMALZ, A. KNECHT and R. PÄSSLER, *J. Appl. Phys.*, 1995, **77**, (6), 2495-2500

The electrical and optical properties of defects due to ion implantation of Ru in Si were studied by using junction space-charge techniques. Two energy levels were observed with energy positions at $E_c - 0.184$ eV (*A*-level) and $E_c + 0.265$ eV (*B*-level), respectively, at 77 K. The changes in enthalpy resulting from the capture of electrons and holes were -8 meV (*A*-level) and 1 meV (*B*-level), respectively. Gibbs' free energies at different temperatures were calculated for both levels. A model for the origin of the observed defects is discussed.

Conduction Mechanisms in RuO_2 -Glass Composites

N. NICOLOSO, A. LECORRE-FRISCH, J. MAIER and R. J. BROOK, *Solid State Ionics*, 1995, **75**, 211-216

The correlation between microstructure and electrical transport in RuO_2 -glass composites with metal oxide volume fractions 0.01-0.4 was studied by SEM, HREM and temperature, frequency and electric field dependent conductivity studies. At high RuO_2 fractions $\geq 20\%$ a metallic conduction mechanism was identified, but at low RuO_2 contents $\leq 3\%$ ionic transport dominated. A quantitative description of electrical transport in RuO_2 -glass composites is presented.

CHEMICAL COMPOUNDS

Highly Reactive Platinum(0) Carbene Intermediates in the Reactions of Diazo Compounds. A Fast Atom Bombardment Mass Spectrometric Study

R. BERTANI, R. A. MICHELIN, M. MOZZON, P. TRALDI, R. SERAGLIA, M. DE F. C. G. DA SILVA and A. J. L. POMBEIRO, *Organometallics*, 1995, **14**, (1), 551-554

A direct reaction of $[\text{Pt}(\text{CH}_2=\text{CH}_2)(\text{PPh}_3)_2]$ (1) with $\text{N}_2\text{CHCO}_2\text{Et}$, under a fast atom bombardment matrix, yielded molecular ions corresponding to the species $[\text{Pt}\{\text{N}_2\text{C}(\text{H})\text{CO}_2\text{Et}\}(\text{PPh}_3)_2]$, $[\text{Pt}\{\text{C}(\text{H})\text{CO}_2\text{Et}\}(\text{PPh}_3)_2]$ and $[\text{Pt}\{\text{C}(\text{H})\text{CO}_2\text{Et}\}(\text{PPh}_3)_2]_2$, which are intermediates in the formation of the fumarate Pt(0) derivative $[\text{Pt}\{\text{trans-C}(\text{H})\text{CO}_2\text{Et}=\text{C}(\text{H})\text{CO}_2\text{Et}\}(\text{PPh}_3)_2]$. (1) was active in the cyclopropanation of styrene in the presence of $\text{N}_2\text{CHCO}_2\text{Et}$.

The Cossee Mechanism: Migratory Insertion Reactions in Palladium Phosphine-Phosphinite Complexes

P. W. N. M. VAN LEEUWEN and K. F. ROOBEK, *Recl. Trav. Chim. Pays-Bas*, 1995, **114**, (2), 73-75

Methyl Pd complexes containing phosphine-phosphinite bidentate ligands containing two P atoms which are only slightly inequivalent undergo stepwise insertions of CO and norbornadiene. The ³¹P NMR spectra showed that a true migration pathway is the main mechanism in this reaction. The large chemical shift difference between the two P atoms allows studies of the intimate mechanism of multiple migratory insertions in 4-co-ordinate complexes.

Synthesis and Properties of Cationic Organopalladium Complexes. Remarkable Rate Enhancement in Olefin Insertion into the Palladium-Aryl Bond by the Generation of a Cationic Palladium Complex from *trans*- $[\text{PdBr}(\text{Ph})(\text{PMe}_3)_2]$

F. KAWATAKA, I. SHIMIZU and A. YAMAMOTO, *Bull. Chem. Soc. Jpn.*, 1995, **68**, (2), 654-660

Pd complexes *trans*- $[\text{PdPh}(\text{py})(\text{PMe}_3)_2]\text{BF}_4$ and *trans*- $[\text{PdPh}(\text{solvent})(\text{PMe}_3)_2]\text{BF}_4$ were obtained by removing the bromide ligand in *trans*- $[\text{PdBr}(\text{Ph})(\text{PMe}_3)_2]$ (1) by AgBF_4 in the presence and absence of pyridine, pyridine-co-ordinated and solvent-co-ordinated cationic complexes. The cationic phenyl Pd complexes have greater reactivities than the parent neutral complex (1) toward olefins to give phenylated olefins by insertion followed by β -H elimination processes. A cationic aryl Pd complex is generated with a vacant site for olefin insertions.

A Novel Route to Dinuclear Heteroleptic Rhodium(III) Complexes of 1,4,7-Trithiacyclononane

H.-J. KIM, J.-H. LEE, I.-H. SUH and Y. DO, *Inorg. Chem.*, 1995, **34**, (4), 796-801

A novel route to dinuclear Rh(III) complex cations with 1,4,7-trithiacyclononane (9S3): $[\text{9S3Rh}(\mu\text{-SPh})_2\text{MCp}^*]^{2+}$, where M = Rh, Ir; $\text{Cp}^* = \text{C}_5(\text{CH}_3)_5$, is described using $[\text{Rh}(\text{9S3})(\text{CO})(\text{PPh}_3)]^+$ (1) as a synthon. (1) is reactive toward oxidative decarbonylation reactions forming a new oxidative addition product with I_2 , $[\text{Rh}(\text{9S3})(\text{PPh}_3)(\text{I})_2]^+$ in good yield. In the presence of excess benzenethiol and NEt_3 , the reaction gives an insoluble red neutral solid $\text{Rh}(\text{9S3})(\text{SPh})_2\text{CH}_2\text{CN}$, which is a potential synthon in the formation of a new class of dinuclear 9S3 complexes.

Dramatic Acceleration of Migratory Insertion in $[\text{MeIr}(\text{CO})_2\text{I}_3]$ by Methanol and by Tin(II) Iodide

J. M. PEARSON, A. HAYNES, G. E. MORRIS, G. J. SUNLEY and P. M. MAITLIS, *J. Chem. Soc., Chem. Commun.*, 1995, (10), 1045-1046

Carbonylation of $[\text{MeIr}(\text{CO})_2\text{I}_3]^+$ to $[\text{MeCOIr}(\text{CO})_2\text{I}_3]$, requires $> 80^\circ\text{C}$ in chlorobenzene, but is greatly accelerated on addition of MeOH by 10^4 at 33°C , or of the Lewis acid SnI_4 by 200 times at 93°C . The acceleration is proposed to arise from activation of an Ir-I bond.

High Oxygen Pressure and the Preparation of New Iridium (VI) Oxides with Perovskite Structure: Sr_2MIrO_6 ($M = \text{Ca}, \text{Mg}$)

D.-Y. JUNG and G. DEMAZEAU, *J. Solid State Chem.*, 1995, 115, (2), 447–455

Ir(VI) in an octahedral co-ordination was stabilised in Sr_2MIrO_6 ($M = \text{Ca}, \text{Mg}$) oxides with an ordered perovskite structure by use of high O pressure. The structure of $\text{Sr}_2\text{CaIrO}_6$ depends strongly on the O pressure and reversibly returns to the original structure according to the heat treatment applied. The oxidation state of Ir is determined and correlated with the structural factors and the covalency of M-O bonds. The electronic configuration of Ir(VI) leads to a high Néel temperature with 55 K (Ca) and 80 K (Mg).

Trans-Cis Isomerization in $[\text{Os}(\text{tpy})(\text{Cl})_2(\text{N})]^+$

D. S. WILLIAMS, G. M. COIA and T. J. MEYER, *Inorg. Chem.*, 1995, 34, (3), 586–592

The Os complex *trans*- $[\text{Os}(\text{tpy})(\text{Cl})_2(\text{N})]\text{Cl}$ (1) was synthesised by adding 2,2',6',2''-terpyridine (tpy) to $[\text{NBu}_4][\text{Os}(\text{N})\text{Cl}_4]$ in dichloromethane and *trans*- $[\text{Os}(\text{tpy})(\text{Cl})_2(\text{N})][\text{PF}_6]$ by addition of $[\text{NH}_4][\text{PF}_6]$ to a methanolic solution of (1). When dissolved in MeOH in the presence of added chloride, (1) slowly isomerised to *cis*- $[\text{Os}(\text{tpy})(\text{Cl})_2(\text{N})]^+$, which was isolated as its $[\text{PF}_6]$ salt. With added chloride, an equilibrium was achieved in the solution between the *trans* and *cis* isomers. Isomerisation did not occur in dichloromethane. A mechanism for isomerisation and substitution is proposed involving associative attack of methanol to form seven-co-ordinate, solvent-bound intermediates, which undergo solvolysis.

A Dihydrogen Complex, $[\text{Os}(\eta^2\text{-H}_2)(\text{CO})\text{-}(\text{quS})(\text{PPh}_3)_2]^+$, in Equilibrium with Its Coordinated Thiol Tautomer ($\text{quS} = \text{quino-line-8-thiolate}$)

M. SCHLAF and R. H. MORRIS, *J. Chem. Soc., Chem. Commun.*, 1995, (6), 625–626

The mixture of two isomers of the new Os complex $\text{Os}(\text{H})(\text{CO})(\text{quS})(\text{PPh}_3)_2$ reacted with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ at -80°C to produce the Os complexes $[\text{Os}(\eta^2\text{-H}_2)(\text{CO})(\text{quS})(\text{PPh}_3)_2]^+$ with dihydrogen *trans* to sulphur or nitrogen along with tautomeric thiol complexes $[\text{Os}(\text{H})(\text{CO})(\text{quSH})(\text{PPh}_3)_2]^+$. The tautomeric equilibria shifted with temperature.

Vertically Linked Ruthenium(II) Porphyrin Oligomers

A. KIMURA, K. FUNATSU, T. IMAMURA, H. KIDO and Y. SASAKI, *Chem. Lett. Jpn.*, 1995, (3), 207–208

A novel porphyrin trimer linked vertically, of formula $\text{Ru}(\text{OEP})(\text{H}_2\text{PyP}_3\text{P})_3$, was synthesised and characterised. The porphyrin ligands with pyridyl groups in these oligomers are perpendicularly co-ordinated to the metal centres of Ru(II) porphyrins. Porphyrin oligomers, $\text{Ru}(\text{OEP})(\text{CO})(\text{H}_2\text{PyP}_3\text{P})$, $\text{Ru}(\text{OEP})(\text{CO})(\text{ZnPyP}_3\text{P})$ and $[\text{Ru}(\text{OEP})(\text{CO})]_2(\text{trans-H}_2\text{Py}_3\text{P}_3)$ were also prepared. This gives a systematic route for constructing perpendicularly linked porphyrin oligomers and polymers and studies of their potential functions are currently in progress.

Synthesis of a [60]Fullerene Derivative Covalently Linked to a Ruthenium(II) Tris(bipyridine) Complex

M. MAGGINI, A. DONÒ, G. SCORRANO and M. PRATO, *J. Chem. Soc., Chem. Commun.*, 1995, (8), 845–846

The synthesis of a [60]fullerene derivative containing the transition metal complex $\text{Ru}(\text{bpy})_3^{2+}$ is described. Its UV-VIS spectrum showed absorptions typical of the two independent chromophores.

ELECTROCHEMISTRY

High Efficiency Electrochemical Reduction of Carbon Dioxide under High Pressure on a Gas Diffusion Electrode Containing Pt Catalysts

K. HARA, A. KUDO, T. SAKATA and M. WATANABE, *J. Electrochem. Soc.*, 1995, 142, (4), L57–L59

The electrochemical reduction of gas phase CO_2 under high pressure (< 50 atm) was performed on a gas diffusion electrode containing Pt electrocatalyst at high current densities. The faradaic efficiency for CO_2 reduction reached 46% at a current density of 900 mA/cm^2 . CH_4 was produced at 35% efficiency.

Fabrication of Highly Dispersed Pt Coated Carbon Electrodes by a Combination of Partial Thermal Decomposition and Electrolytic Reduction of Pt Complex

Y. KAMEGAYA, H. KOBAYASHI and T. MITAMURA, *Denki Kagaku*, 1995, 95, (2), 122–127

A Pt coated electrode was made, using a combination of partial thermal decomposition of $\text{Pt}(\text{NO}_2)_2(\text{NH}_3)_2$ on C paper at 350°C and electrochemical reduction of the Pt complex at 0 V (vs. Ag/AgCl) in a mixed solution of 1 M MeOH and 0.5 M H_2SO_4 at 60°C . The specific surface area and activity of Pt on this electrode was higher than those obtained with H_2PtCl_6 .

Electrochemical Sulphur Dioxide Oxidation with Platinum-Aluminum Electrocatalysts

J. LEE and S. H. LANGER, *J. Appl. Electrochem.*, 1995, 25, (4), 353–357

Pt-Al electrocatalysts supported on C black were studied for electrogenerative SO_2 oxidation in hybrid type, liquid-phase SO_2/O_2 cells. When 1–30 at.% Al was incorporated with Pt electrocatalysts on C, electrocatalytic activity increased for SO_2 oxidation. Even a small amount of Al ~ 1 at.% incorporated in the Pt produced a significant synergistic effect.

Kinetic Properties of a Pt/Lambda-MnO₂ Electrode for the Electroinsertion of Lithium Ions in an Aqueous Phase

H. KANO, Q. FENG, Y. MIYAI and K. OOI, *J. Electrochem. Soc.*, 1995, 142, (3), 702–707

Kinetic properties of a Pt/ λ - MnO_2 electrode for the electrochemical insertion of Li ions were studied in the aqueous phase. The electrochemical insertion reaction of Li ions proceeded in two steps at 0.6–0.98 V (vs. S.C.E.). The chemical diffusion coefficients of Li ions in the MnO_2 were 6.6×10^{-11} – 1.4×10^{-10} cm^2/s .

Preparation of Microparticle Palladium Incorporating Poly[N-(5-hydroxypentyl)-pyrrole] Film-Coated Electrode

N. TAKANO, M. NAKABAYASHI and N. TAKENO, *Chem. Lett. Jpn.*, 1995, (3), 219–220

A new conducting polymer catalytic electrode incorporating Pd microparticles into poly[N-(5-hydroxypentyl)-pyrrole] film-coated electrode was prepared by immersion treatment in Na_2PdCl_4 solution, followed by electrochemical reduction of permeated PdCl_4^{2-} ions in the films. The electrode exhibited catalytic activity for the hydrogenation of acetylene compound.

PHOTOCONVERSION

Effects of H^+ , Cl^- and CH_3COOH on the Photocatalytic Conversion of PtCl_6^{2-} in Aqueous TiO_2 Dispersion

C. XI, Z. CHEN, Q. LI and Z. JIN, *J. Photochem. Photobiol. A: Chem.*, 1995, 87, (3), 249–255

Studies of the effects of H^+ , Cl^- and CH_3COOH (1) on the photocatalytic conversion of PtCl_6^{2-} in an aqueous TiO_2 dispersion showed that the hydrolysis product of PtCl_6^{2-} is photocatalytically converted into a solid deposit on the TiO_2 surface which changes with the degree of the PtCl_6^{2-} hydrolysis. No deposit was observed on the TiO_2 when both H^+ and Cl^- concentrations were high enough to depress the hydrolysis. The effect of (1) on the composition of the photocatalytic product of PtCl_6^{2-} on TiO_2 is closely related to the degree of its ionisation.

Photoinduced Addition of Dioxygen Molecules in the Unsaturated Sites of the $\text{Pd}_3(\text{dppm})_3\text{CO}^{2+}$ Catalyst

P. D. HARVEY, M. CROZET and K. T. AYE, *Can. J. Chem.*, 1995, 73, (1), 123–130

The photoinduced addition of O_2 onto the unsaturated cluster $\text{Pd}_3(\text{dppm})_3\text{CO}^{2+}$ (as a CF_3CO_2^- salt) in acetonitrile is reported. The final product $\text{Pd}_3(\text{dppm})_3(\text{O}_2)_2^{2+}$ is formed in a multi-step in which two photochemical intermediates are observed, such as $\text{Pd}_3(\text{dppm})_3(\text{O}_2)(\text{CO})^{2+}$ and $\text{Pd}_3(\text{dppm})_3(\text{O}_2)^{2+}$. Studies showed that O_2 binds the Pd, centre as a peroxo- O_2 , and acts as a two electron donor that triply bridges the metal atoms, forming a 44-electron cluster.

Photochemistry and C-H Bond Activation Reactivity of $(\text{HBPz}^*)_3\text{Rh}(\text{CO})_2$ ($\text{Pz}^* = 3,5$ -Dimethylpyrazolyl) in Hydrocarbon Solution

A. A. PURWOKO and A. J. LEES, *Inorg. Chem.*, 1995, 34, (2), 424–425

The solution photochemistry of $(\text{HBPz}^*)_3\text{Rh}(\text{CO})_2$ was studied and the absolute quantum efficiencies for intermolecular C-H bond activation at several excitation wavelengths were determined. The C-H bond activation reaction proceeded well and cleanly in room-temperature solutions after photolyses in either the near-UV or visible region. Quantum efficiency data revealed that the C-H bond activation is strongly dependent on the wavelength of light excitation, and that high conversion efficiencies can be obtained.

Electronic Energy Transfer in a Supramolecular Species Containing the $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Os}(\text{bpy})_3]^{2+}$, and Anthracene Chromophoric Units

P. BELSER, R. DUX, M. BAAK, L. DE COLA and V. BALZANI, *Angew. Chem., Int. Ed. Engl.*, 1995, 34, (3), 595–597
A very fast and efficient energy transfer of $4.7 \times 10^8/\text{s}$ was observed from the Ru- to the Os-based moiety in the reaction of the above components. In O_2 , a photoreaction occurred which gave a strong decrease, ~80 times, in the rate of the energy transfer process.

Dramatic Increase of $^3\text{MLCT}$ State Lifetime of a Ruthenium(II) Polypyridine Complex upon Entrapment within Y-Zeolite Supercages

K. MARUSZEWSKI and J. R. KINCAID, *Inorg. Chem.*, 1995, 34, (8), 2002–2006

Entrapment of $\text{Ru}(\text{bpy})_2(\text{daf})^{2+}$, where daf is diazafluorene, in zeolite Y supercages induced a dramatic increase in the excited-state lifetime and emission intensity compared to solutions of the complex. The observed temperature dependence of the excited-state lifetime was modelled by a kinetic equation with two thermal terms corresponding to the so-called fourth $^3\text{MLCT}$ state and ligand field (LF) state, respectively. The increased lifetime of the entrapped complex was found to result from zeolite-induced destabilisation of the LF state.

Photoadduct between Tris(1,4,5,8-tetraaza-phenanthrene)ruthenium (II) and Guanosine Monophosphate—a Model for a New Mode of Covalent Binding of Metal Complexes to DNA

L. JACQUET, J. M. KELLY and A. KIRSCH-DE MESMAEKER, *J. Chem. Soc., Chem. Commun.*, 1995, (9), 913–914
 $\text{Ru}(\text{TAP})_2(2\text{-TAP-G})^{2+}$ ($\text{TAP} = 1,4,5,8$ -tetraaza-phenanthrene), in which the guanine moiety is bound via N-2 to C-2 of one of the TAP ligands, was produced by visible light irradiation of $[\text{Ru}(\text{TAP})_3]^{2+}$ in aqueous solutions containing 5'-guanosine-monophosphate (GMP) and subsequent treatment with HCl. The reaction is said to proceed by initial oxidation of the guanine by the Ru complex excited state, subsequent proton transfer (both processes were verified by laser flash photolysis) and subsequent coupling of the radicals that were formed.

ELECTRODEPOSITION AND SURFACE COATINGS

Fabrication of Ultrathin Metallic Membranes on Ceramic Supports by Sputter Deposition

V. JAYARAMAN, Y. S. LIN, M. PAKALA and R. Y. LIN, *J. Membrane Sci.*, 1995, 99, (1), 89–100

Ultrathin Pd films (< 500 nm) grown on porous ceramic supports were prepared by sputter deposition. Fairly gas-tight Pd films with good adhesion could be coated on sol-gel derived fine pore $\gamma\text{-Al}_2\text{O}_3$ supports but not on coarse $\alpha\text{-Al}_2\text{O}_3$. Both coating temperature and substrate type affect the grain size, N gas-tightness and the adhesion of the deposited metallic films. The optimum coating temperature is 400°C.

Effect of KCl Concentration on Activation Using Pd-Sn(II) Chloride Solutions

E. D. DOBREVA, A. L. LIRKOV, A. T. TRANDAFILOV and L. I. PINDEVA, *Galvanotechnik*, 1995, **86**, (2), 560–566
Formation of Pd nuclei on the surface of plastics using colloidal activating solutions strongly acidified with HCl is compared with results obtained using weak HCl with a KCl based activator. The effect of temperature increase and modification of the HCl and KCl concentration on the activation performance are examined. The greatest Pd adsorption was obtained using solutions with concentrated HCl. Results were obtained by measurement of surface tension, contact angle, and radiochemical and SEM-based methods.

Electrodeposition of Ru-Sn Coatings

D. R. HODGSON, *J. Mater. Sci. Lett.*, 1995, **14**, (4), 275
Ru-Sn plating solutions containing RuCl₃ and SnCl₄·5H₂O dissolved in H₂SO₄ were prepared and electrodeposition was carried out at room temperature using a Pt mesh anode surrounding a Ti cathode, at a constant current density of 30 mA/cm², for various times. Coatings were deposited onto a Ti strip, previously etched in oxalic acid. A dramatic increase in durability was observed after heating the deposits from a solution containing Ru 0.009 mol/dm³ and Sn 0.19 mol/dm³, in air for 1 h at 500°C. This method is fast and the deposits become more stable by heating in air.

APPARATUS AND TECHNIQUE

A Method for Preparation of Pt-Ir Tips for the Scanning Tunneling Microscope

V. WEINSTEIN, M. SLUTZKY, A. ARENSHTAM and E. BEN-JACOB, *Rev. Sci. Instrum.*, 1995, **66**, (4), 3075–3076
Pt-Ir tips for STM were prepared by AC etching of Pt-Ir specimens, using Pt₀,Ir₀, wire of diameter 0.25 mm, in 1–2 M NaOH + saturated NaOCN distilled H₂O solution. The optimal frequency was ~ 400 Hz and the etching duration was about 30 min. This method is simple, relatively fast, taking ~ 35–40 min per tip, and produces tips with a small opening angle.

Application of Redox Cycling Enhanced Current at an Interdigitated Array Electrode for Iron-Trace Determination in Ultrapure Spectral Carbon

D. BUSTIN, S. MESÁROS, P. TOMČÍK, M. RIEVAJ and V. TVAROZEK, *Anal. Chim. Acta*, 1995, **305**, (1–3), 121–125

Vertically arranged interdigitated array (IDA) electrodes, containing a continuous Pt-film base and a 0.5 µm thick insulation layer in the middle separating the upper Pt-IDA electrodes from the Pt-base, were used for Fe trace analysis in ultrapure spectral C. The spiked samples were used during tests and the results were compared with those obtained by AAS. The redox cycling enhanced the electrochemical signal of the IDA microelectrode, and the IDA signal was obtained for 1×10^{-3} – 1.5×10^{-4} wt.% Fe. The method is a less expensive alternative to the AAS determination of Fe pollutants in ultrapure carbon.

Electrochemical Removal of Both NO and CH₄ under Lean-Burn Conditions

T. HIBINO, *J. Appl. Electrochem.*, 1995, **25**, (3), 203–207
An electrochemical cell Pd/YSZ/Pd of simple structure and small size was placed in a flow of NO and CH₄ mixture at 650–750°C with direct current. Both NO and CH₄ were removed, even in the presence of excess O₂. No deterioration of activity was found in the presence of H₂O and CO₂. NO was reduced to N₂ at the cathode, and CH₄ was oxidised to CO_x at both the anode and cathode. At the cathode, the reduction of NO and the oxidation of CH₄ proceeded with the removal of chemisorbed O species from the Pd surface, and at the anode, the oxidation of CH₄ was increased by forming an active O atom.

Characterization of Nanocrystalline Palladium for Solid State Gas Sensor Applications

F. A. VOLKENING, M. N. NAIDOO, G. A. CANDELA, R. L. HOLTZ and V. PROVENZANO, *NanoStructured Mater.*, 1995, **5**, (3), 373–382

Nanocrystalline Pd was prepared by the inert gas condensation technique, consolidated into pellets, and characterised. The H gas absorption/desorption properties of the nanocrystalline Pd were studied to show their application to solid state gas sensor development. The nanocrystalline materials exhibited fast response to H₂ and complete recovery up to an exposure to several % of H. Studies showed that the dissociative chemisorption of H on the surface of the Pd is the rate controlling step for absorption, while desorption was controlled by diffusion of H out of the Pd metal.

Highly Selective Biosensing of Lactate at Lactate Oxidase Containing Rhodium-Dispersed Carbon Paste Electrodes

J. WANG, Q. CHEN and M. PEDRERO, *Anal. Chim. Acta*, 1995, **304**, (1), 41–46

A highly selective lactate biosensor based on the immobilisation of lactate oxidase within a Rh-dispersed C paste is presented. The amperometric biosensing of lactate can be performed at low operating potentials. The effective catalytic action of the Rh microparticles towards the generated H₂O₂ or consumed O₂ allows tuning of the operating potential to a region which prevents unwanted reactions. The detection limit was 1.5×10^{-7} M and the response time 8 s. A fast and sensitive flow injection operation is obtained.

Design and Optimization of a Selective Subcutaneously Implantable Glucose Electrode Based on “Wired” Glucose Oxidase

E. CSÖREGI, D. W. SCHMIDTKE and A. HELLER, *Anal. Chim. Acta*, 1995, **67**, (7), 1240–1244

An implantable 0.29 mm wide flexible wire electrode for glucose monitoring contains 3 layers with no leachable components: a “wired” glucose oxidase (GOX) sensing layer formed by cross-linking {poly[(1-vinylimidazolyl)Os(4,4'-dimethylbipyridine)₂Cl]}²⁺ and GOX with poly(ethylene glycol) diglycidyl ether, a mass transport limiting layer, and a non-fouling biocompatible layer. When poised at +200 mV vs S.C.E. and at 37°C, the electrode had in vitro sensitivity of 1–2.5 nA/mM.

JOINING

Thin Multilayer Palladium Coatings for Semiconductor Packaging Applications. Part I: Solderability

I. V. KADIJA, J. A. ABYS, J. J. MAISANO, E. J. KUDRAK and S. SHIMADA, *Plat. Surf. Finish.*, 1995, **82**, (2), 56–62
Physical and chemical characteristics of Pd and Pd alloy electrodeposits were studied to find their performance as solderable and wire-bondable materials. The most stringent soldering requirements were met by combining layers with limiting porosity, inhibiting thermal diffusion and increasing wetting speeds. Combinations of Pd and Pd alloys with thin Au flash showed good solderability and wire bonding. Pd finishes have superior bond strength than Sn-Pb ones.

HETEROGENEOUS CATALYSIS

Investigation of Methane Oxidation on Pt/Al₂O₃ Catalysts under Transient Reaction Conditions

R. BURCH and P. K. LOADER, *Appl. Catal. A: Gen.*, 1995, **122**, (2), 169–190

The oxidation of CH₄ on Pt/Al₂O₃ catalysts was studied using various gas mixtures as a function of the state of oxidation or reduction of the Pt surface. The activity for CH₄ oxidation increased sharply after addition of the reactants to either a pre-reduced or a pre-oxidised catalyst. Even after re-oxidation at 300°C, the Pt particles had a strong “memory” of previous reduction treatments, and the position of the maximum activity was reproducible for pre-reduced catalysts.

A New Class of Chiral Modifiers for the Enantioselective Hydrogenation of α -Ketoesters with Pt/Al₂O₃

K. E. SIMONS, G. WANG, T. HEINZ, T. GIGER, T. MALLAT, A. PFALTZ and A. BAIKER, *Tetrahedron: Asymmetry*, 1995, **6**, (2), 505–518

A series of enantiomerically pure chiral amino alcohols was prepared and applied as modifiers in the enantioselective hydrogenation of ethyl pyruvate over Pt/Al₂O₃ catalysts. Their use allowed an enantiomeric excess of $\leq 75\%$ to be obtained. A molecular model of the modifiers and reactant on a Pt(111) surface explained the observed enantiodifferentiation.

Increased Aromatization in the Reforming of Mixtures of *n*-Hexane, Methylcyclopentane and Methylcyclohexane over Composites of Pt/BaKL Zeolite with Pt/ β or Pt/USY Zeolites

P. G. SMIRNIOTIS and E. RUCKENSTEIN, *Appl. Catal. A: Gen.*, 1995, **123**, (1,2), 59–88

The performance of the individual L, β and USY zeolites supporting Pt and of composites of Pt/BaKL with either Pt/ β or Pt/USY was studied during reforming of *n*-hexane, methylcyclopentane, or methylcyclohexane. The increase of the Pt loading increased the aromatic selectivity for the hydrocarbons. Reactions over the composites gave increased selectivities for C ≥ 7 aromatics. This is attributed to the synergism caused by the components of the composites in combination with components of the feed mixture.

The Preparation of High-Surface-Area Pt/SiO₂ Catalysts with Well-Defined Pore Size Distributions

W. ZOU and R. D. GONZALEZ, *J. Catal.*, 1995, **152**, (2), 291–305

Thermally stable supported Pt catalysts were prepared by matching the metal particle size to the average pore diameter. In the 3–8 pH range, blank SiO₂ gels prepared using tetraethoxysilane (TEOS) had BET surface areas of 350–800 m²/g and mesoporous structures with an average pore diameter of 4–25 nm at a constant H₂O:TEOS ratio of 10. The use of Pt(AcAc)₂ resulted in average pore diameters of 4–20 nm by adjusting the H₂O:TEOS ratio during synthesis. Catalytic activities were found to be comparable or slightly superior to supported metal catalysts prepared by traditional methods.

Synthesis of a Highly Active Superacid of Platinum-Supported Zirconia for Reaction of Butane

M. HINO and K. ARATA, *J. Chem. Soc., Chem. Commun.*, 1995, (7), 789–790

A highly active superacid of 8 wt. % Pt/ZrO₂ was obtained for the skeletal isomerisation of butane to isobutane by impregnating ZrO₂ gel with 0.5 mol/dm³ H₂SO₄ followed by drying. The sulphated gel was impregnated with H₂PtCl₆ solution and calcined in air at 600°C. The catalytic activity achieved was the greatest of any solid catalyst yet reported for the acid-catalysed isomerisation of butane without reducing the catalyst before use or in the absence of H₂.

Effects of Modification of Pd/SiO₂ with Rh on Catalytic Activity for Ethene Hydroformylation

N. TAKAHASHI, J. SAKAUCHI, T. KOBAYASHI and H. LI, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, (8), 1271–1276

The catalytic activity of Pd/SiO₂ catalysts modified with Rh was studied during ethene hydroformylation using Pd catalysts with high (1) or low dispersions. The activity for propionaldehyde formation on (1) catalyst modified with Rh(CH₃CO₂)₂ at Rh:Pt = 1.0 was very high, being about 4 times that on unmodified (1) or more than 50 times that on Rh/SiO₂ containing the same amount of Rh alone. This remarkable increase in activity is probably due to the formation of a Rh-Pd bimetallic structure at the surfaces of metal particles.

Catalytic Properties of Nanocrystalline WO_{3-x}, Pt/WO_{3-x}, and Pd/WO_{3-x} Particles

H.-M. LIN, C.-Y. TUNG, C.-M. HSU and P.-Y. LEE, *J. Mater. Res.*, 1995, **10**, (5), 1115–1119

Nanocrystalline (NC) WO_{3-x}, Pt/WO_{3-x} and Pd/WO_{3-x} catalysts showed good interfacial bonding between NC Pt or Pd and WO_{3-x} particles. The nanocrystals WO_{3-x}, Pt/WO_{3-x} and Pd/WO_{3-x} grew into needle shapes with a plate structure inside after sintering at 900°C, to form a network structure. However, the mean particle size of nanophase Pt and Pd increases only from < 10 nm to 30 nm and 50 nm, respectively. The results of CO oxidation show that nanophase Pt/WO_{3-x} powders have better catalytic effects on converting CO to CO₂ than nanophase WO_{3-x} and Pd/WO_{3-x} powders.

Selective Hydrogenation of Phenylacetylene on Pumice-Supported Palladium Catalysts

D. DUCA, L. F. LIOTTA and G. DEGANELLO, *J. Catal.*, 1995, 154, (1), 69–79

The behaviour of Pd/pumice catalysts during the above reaction in the liquid phase, was studied for a large range of metallic dispersions. The hydrogenation was "structure insensitive". Pd/pumice catalysts show high activity and selectivity at high metal dispersions, so they can be used in industrial applications.

New Catalyst Precursors Constituted of AsPh₃ and Palladium on Carbon or Palladium(II) Acetate as Efficient Promoters of Selective Cross-Coupling Reactions between Functionalized Alkenyl Halides and Aryl- or 1-Alkynylzinc Chlorides

R. ROSSI, F. BELLINA, A. CARPITA and R. GORI, *Synlett*, 1995, (4), 344–346

Catalyst precursor containing a mixture of Pd/C and AsPh₃, and also that obtained by treatment of Pd(OAc)₂ with AsPh₃ in THF at 60°C were found to promote efficient cross-coupling reactions between aryl- or 1-alkynylzinc chlorides and alkenyl halides. The latter contain an electron-withdrawing substituent linked to their C-C double bond.

One-Step Synthesis of PdSAPO-5 Catalysts and Their Structure

T.-C. XIAO, L.-D. AN, H.-L. WANG, F. DENG, N.-H. YANG and J.-Q. QIU, *Chin. J. Catal.*, 1995, 16, (2), 108–113

PdSAPO-5 bifunctional catalysts were prepared by direct addition of Pd to the reactant gel mixture of silicoaluminophosphate followed by their modification. The addition of H₂PdCl₂ did not depress the yield of SAPO-5 and the Pd could be evenly dispersed in the channels of PdSAPO-5(Cl). The dispersion of Pd in PdSAPO-5 was much better than that in Pd/SAPO-5 prepared by impregnation.

[Ru₆(CO)₁₈]²⁻ in NaX Zeolite Cages: Characterization by EXAFS and FTIR Spectroscopy

A.-M. LIU, T. SHIDO and M. ICHIKAWA, *J. Chem. Soc., Chem. Commun.*, 1995, (5), 507–508

Ru^{III}(NH₃)₆ in the cages of NaX zeolite was converted into the Ru carbonyl cluster dianion [Ru₆(CO)₁₈]²⁻ in the presence of CO + H₂, which was reversibly fragmented and reconstructed under oxidative and reductive conditions, respectively. The structure of this Ru cluster was very sensitive to O₂.

New Supported [Ru₆N] Clusters as a Potential Transition Metal Nitride Catalyst

Y. IZUMI and K.-I. AIKA, *Chem. Lett. Jpn.*, 1995, (2), 137–138

[Ru₆N] cluster catalysts were prepared by reacting [Ru₆N(CO)₁₆]⁻ clusters with MgO, K⁺-doped MgO or Cs⁺-doped MgO. The [Ru₆N] unit remained in reaction conditions and showed higher activities in NH₃ synthesis than conventional Ru catalysts or Ru clusters prepared from [Ru₆C(CO)₁₆Me]⁻ or [Ru₆(CO)₁₈]²⁻ complexes.

HOMOGENEOUS CATALYSIS

Highly Stereoselective Allylation of Benzaldehyde: Generation of a Stereochemically Defined Allylzinc Species from a π -Allylpalladium Intermediate and Diethylzinc

Y. TAMARU, A. TANAKA, K. YASUI, S. GOTO and S. TANAKA, *Angew. Chem., Int. Ed. Engl.*, 1995, 34, (7), 787–789

The stereoselective addition of 2-cyclohexenylzinc species, generated by the Pd⁰-catalyzed reaction of 2-cyclohexenyl esters and diethylzinc, to benzaldehyde using Pd(PPh₃)₄ catalyst is reported. The Pd-catalyzed allylation had the excellent stereoselectivity of *syn* addition with inversion of the allylic stereocentre for 2-cyclohexenyl substrates and (*Z*)-*anti* addition for acyclic 1,3-disubstituted allylic substrates. This technique can be applied to a range of allylic substrates prepared from allylic alcohols and α,β -unsaturated aldehydes.

Homogeneous Multimetallic Catalysts. 11. Carbonylation of Aryl Iodides with HSiEt₃ Catalyzed by Pd-Co Bimetallic Systems

Y. MISUMI, Y. ISHII and M. HIDAI, *Organometallics*, 1995, 14, (4), 1770–1775

The bimetallic catalysts PdCl₂(PPh₃)₂-Ru(CO)₁₂ or PdCl₂(PPh₃)₂-Co₂(CO)₈ were found to be effective for carbonylation of aryl iodides and HSiEt₃ to yield benzyl silyl ether as the main product, although they were not active individually. Addition of NEt₃ to the Pd-Co mixed-metal-catalyzed carbonylation greatly changed the selectivity of the products giving 1,2-diaryl-1,2-disiloxyethane as the major product. Detailed mechanisms are proposed for this reaction.

A Simple, Effective, New, Palladium-Catalyzed Conversion of Enol Silanes to Enones and Enals

R. C. LAROCK, T. R. HIGHTOWER, G. A. KRAUS, P. HAHN and D. ZHENG, *Tetrahedron Lett.*, 1995, 36, (14), 2423–2426

Enol silanes obtained from aldehydes and ketones were easily converted to the corresponding α,β -unsaturated carbonyl compounds by 10% Pd(OAc)₂ in the presence of 1 atm O₂ in dimethylsulphoxide as the solvent. The process requires no additional reagents or reoxidants for Pd, so is environmentally attractive and should therefore find widespread use.

Palladium-Catalysed Carbonylation of Halogenoalkynes to Alkynylcarboxylic Acid Esters under Mild Conditions

T. T. ZUNG, L. G. BRUK, O. N. TEMKIN and A. V. MALASHKEVICH, *Mendeleev Commun.*, 1995, (1), 3–4

Alkynylcarboxylic acid esters were formed by Pd-catalysed carbonylation of bromoalkynes, iodoalkynes and σ -alkynyl Pd(II) complexes under CO at atmospheric pressure. Et₃N or NaOAc may be added to the methanol solution of PdX₂-LiX (X = Br, I) catalyst. Esters were produced in high yield and under mild reaction conditions at 40°C. Ester formation must occur from iodoalkyne as an intermediate product.

Novel Palladium-Catalysed Cyclodimerization of Butadiene in the Presence of Carbon Dioxide and Water

F. BERGAMINI, F. PANELLA, R. SANTI and E. ANTONELLI, *J. Chem. Soc., Chem. Commun.*, 1995, (9), 931–932
A Pd-catalysed cyclodimerisation of butadiene to 2-vinylmethylenecyclopentane occurring in catalytic turnovers and giving yields much superior to those of the Ni-based systems, which are specific for cyclodimerisation reactions, is reported. The system used Pd(O)L_n (L = Ph₃P, (*o*-tolyl)₃P), CO₂ and H₂O.

Hydroesterification of Olefins Catalyzed by Pd(OAc)₂ Immobilized on Montmorillonite

C. W. LEE and H. ALPER, *J. Org. Chem.*, 1995, 60, (1), 250–252

Pd acetate immobilised on montmorillonite was found to be an efficient catalyst for the hydroesterification of olefins with CO and CH₃OH, in the presence of PPh₃ and an acid promoter, giving branched chain esters in good yields and selectivities. The reaction was regioselective for aryl olefins and vinyl benzoate, and regioselective for aliphatic olefins.

Palladium(0)-Catalyzed Phenylation of Imidazo[4,5-*b*]pyridines

S. GRIVAS and S. LINDSTRÖM, *J. Heterocyclic Chem.*, 1995, 32, (2), 467–471

Coupling of benzeneboronic acid with 2-chloro, 6-bromo and 6-bromo-2-chloro derivatives of 1- and 3-methylimidazo[4,5-*b*]pyridines was catalysed by Pd(PPh₃)₄ to novel 2-phenyl-, 6-phenyl- and 2,6-diphenylimidazo[4,5-*b*]pyridines. The phenylation of imidazo[4,5-*b*]pyridines containing labile H was unsuccessful.

Rhodium-Catalyzed Intramolecular Silylformylation of Acetylenes: A Vehicle for Complete Regio- and Stereoselectivity in the Formylation of Acetylenic Bonds

F. MONTEIL, I. MATSUDA and H. ALPER, *J. Am. Chem. Soc.*, 1995, 117, (15), 4419–4420

Regio- and stereospecific intramolecular silylformylation of acetylenic bonds was studied in the presence of a Rh complex catalyst. Reaction of pent-4-ynylmethylphenylsilane with CO and a catalytic amount of either the zwitterionic Rh complex (η⁵-C₅H₅BPh₃)Rh⁺ (1,5-COD) (COD = cyclooctadiene) or Rh₂(CO)₁₂ and triethylamine gave the corresponding aldehyde in 43% and 56% isolated yield, respectively. The six-membered ring silacycles were isolated in higher yields than their five-membered counterparts.

Asymmetric Hydrosilylation of Keto Esters Catalyzed by a Rhodium Complex with Trans-Chelating Chiral Diphosphine EtTRAP

M. SAWAMURA, R. KUWANO, J. SHIRAI and Y. ITO, *Synlett*, 1995, (4), 347–348

Asymmetric hydrosilylation of α-, β- and γ-keto esters with diphenylsilane in the presence of 1 mol% Rh catalyst, such as [Rh(COD)]₂BF₄, containing *trans*-chelating chiral phosphine ligand EtTRAP gave optically active alcohols with enantiomeric excesses of 32–93%.

Use of the Redox-Active Ligand 1,1'-Bis(diphenylphosphino)cobaltocene to Reversibly Alter the Rate of the Rhodium(I)-Catalyzed Reduction and Isomerization of Ketones and Alkenes

I. M. LORKOVIC, R. R. DUFF and M. S. WRIGHTON, *J. Am. Chem. Soc.*, 1995, 117, (12), 3617–3618

The synthesis and characterisation of the reversibly redox-active hydrogenation catalyst precursor [Rh(dppc)NBD]^{2+/+}(PF₆)₂ (1) (NBD = bicyclo[2.2.1]-hepta-2,5-diene, dppc = 1,1'-bis(diphenylphosphino)cobaltocene) is reported. (1) reacts in both states of charge with H₂ in acetone to give [Rh(dppc)-(acetone)_n]^{2+/+} (2). Studies of the effect of changes in the ligand state of charge on catalytic activity showed that between the two states of charge of (2), (2)_{ox} is the faster and more durable hydrosilylation catalyst, while (2)_{red} is the faster hydrogenation catalyst.

Rhodium Catalysed Asymmetric Hydroformylation with Diphosphite Ligands Based on Sugar Backbones

G. J. H. BUISMAN, M. E. MARTIN, E. J. VOS, A. KLOOTWIJK, P. C. J. KAMER and P. W. N. M. VAN LEEUWEN, *Tetrahedron: Asymmetry*, 1995, 6, (3), 719–738

Chiral diphosphite ligands (PP) prepared from (2,2'-biphenyl-1,1'-diyl), etc., and sugar backbones were used in the Rh catalysed asymmetric hydroformylation of styrene. Enantioselectivities ≤ 64% were obtained with stable HRhPP(CO)₂ catalysts. High regioselectivity to the branched aldehyde was found at relatively mild reaction conditions at 25–40°C and 9–45 bar of syngas pressure. A relationship was found between the trigonal bipyramidal structure and the enantioselectivity of the HRhPP(CO)₂.

Hydrosilylation of Phenylacetylene Catalyzed by [Ir(COD)(η²-*i*-Pr₂PCH₂CH₂OMe)](BF₄)

M. A. ESTERUELAS, M. OLIVAN, L. A. ORO and J. I. TOLOSA, *J. Organomet. Chem.*, 1995, 487, (1–2), 143–149

The cationic complexes [Ir(diolefin)(η²-*i*-Pr₂PCH₂CH₂NMe₂)](BF₄) (diolefin = 1,5-cyclooctadiene or tetrafluorobenzobarrelene) and [Ir(diolefin)(η²-*i*-Pr₂PCH₂CH₂OMe)](BF₄) catalyse the reaction of phenylacetylene with triethylsilane to give PhCH=CH₂, PhC=CSiEt₃, *cis*-PhCH=CH(SiEt₃), *trans*-PhCH=CH(SiEt₃) and Ph(SiEt₃)C=CH₂. Under catalytic conditions both hydridoalkynyl and hydridosilyl intermediates are formed.

Aromatic Hydrogen Isotope Exchange Reactions Catalysed by Iridium Complexes in Aqueous Solution

C. A. LUKEY, M. A. LONG and J. L. GARNETT, *Aust. J. Chem.*, 1995, 48, (1), 79–91

Ir chloro complexes in aqueous acetic acid solution are active catalysts for H isotope exchange in aromatic compounds. The optimum conditions for exchange were found at 0.02 M catalyst concentration in a solvent consisting of 50 mol % acetic acid/H₂O, at 160°C when the exchange rate was significant and precipitation of Ir metal was minimised. The active catalyst for both systems is a solvated Ir(III) specie.

Ruthenium-Catalyzed Synthesis of Butenolides and Pentenolides via Contra-Electronic α -Alkylation of Hydroxyalkynoates

B. M. TROST, T. J. J. MÜLLER and J. MARTINEZ, *J. Am. Chem. Soc.*, 1995, 117, (7), 1888–1899

The addition of alkenes to 4-hydroxy-2-alkynoates in an Alder-ene type mode yielded butenolides in the presence of CpRu(COD)Cl, which was the most effective catalyst, in aqueous DMF or MeOH when the reaction proceeded with excellent chemoselectivity. Ru catalysts changed the rules of selectivity with respect to regioselectivity, when the usual preference for β -alkylation is reversed and α -alkylation becomes predominant. Acetogenin (+)-ancepsenolide was obtained from commercially available 10-undecenal and methyl (S)-lactane in seven steps with 31% overall yield.

Catalytic Addition of Aromatic Carbon-Hydrogen Bonds to Olefins with the Aid of Ruthenium Complexes

F. KAKIUCHI, S. SEKINE, Y. TANAKA, A. KAMATANI, M. SONODA, N. CHATANI and S. MURAI, *Bull. Chem. Soc. Jpn.*, 1995, 68, (1), 62–83

Ru(H)₂(CO)(PPh₃)₃ catalysed the addition of *ortho* C-H bonds of aromatic ketones to olefins with a high efficiency and selectivity. 2'-Methylacetophenone reacted with terminal olefins to give 1:1 coupling products in good to excellent yields. Acetylnaphthalenes, cyclic aromatic ketones and heteroaromatic ketones also reacted with triethoxyvinylsilane to give 1:1 addition products in nearly quantitative yields.

GLASS TECHNOLOGY

Platinum Tube Feeder Aids Holloware Forming

E. SCHÖTZ, *Glass*, 1995, 72, (5), 181–182; 185–186
Development in feeder tube technology showed the advantages of using a Pt tube feeder with an agitator chamber, for processing special glasses which are chemically highly homogeneous. The increased demand for quality, and the reduction in cost, is making the use of Pt feeders for mass-produced container or domestic glassware very important.

ELECTRICAL AND ELECTRONIC ENGINEERING

Highly Reproducible Fabrication Technology for Passivated AlGaAs/GaAs Heterojunction Bipolar Transistors with Pt/Ti/Pt/Au Base Electrodes

S. HONGO, T. SUGIYAMA, Y. KURIYAMA, N. IIZUKA and M. OBARA, *Jpn. J. Appl. Phys.*, 1995, 34, (2B), 1181–1184
A highly reproducible fabrication technology for passivated heterojunction bipolar transistors has been developed using a thermally stable Pt/Ti/Pt/Au base electrode. Metal penetrates through the Al_{0.3}Ga_{0.7}As emitter layer to contact the base layer. A citric acid based selective etchant is used to allow the reproducibility of passivation layer thickness. The excess base leakage current density was reduced to ~ 1 μ A/ μ m.

Direct Liquid Injection MOCVD of High Quality PLZT Films

W. TAO, S. B. DESU and T. K. LI, *Mater. Lett.*, 1995, 23, (4, 5, 6), 177–180

High quality La-modified lead zirconate titanate (PLZT) which has excellent ferroelectric properties for non-volatile memory was deposited as films on (111)Pt/Ti/SiO₂/Si substrates by direct liquid injection metal-organic chemical vapour deposition. The as-deposited PLZT films had smooth, reflective surfaces. XRD studies showed a single perovskite phase with *a*-axis oriented PLZT films formed in situ at a substrate temperature of 650°C. Electrical fatigue tests showed 70% of the original switched polarisation still remained after 1 \times 10¹⁰ cycles.

Magnetoresistance and Interlayer Coupling in Co-Pt/Cu/Permalloy Sandwiches

K. KATO, O. KITAKAMI and Y. SHIMADA, *Jpn. J. Appl. Phys.*, 1995, 34, (2A), 492–496

Addition of a small amount of Pt (~ 5.5 at.%) greatly improved the magnetic hardness of very thin Co films. Co-Pt/Cu/permalloy sandwiches were prepared by combination of the hard Co_{94.3}Pt_{5.5} film with a soft permalloy film. The sandwiches exhibited a large magnetoresistance of \leq 4.4% without any buffer underlayers, but the magnetisation reversal field of the permalloy layer was increased due to the ferromagnetic interlayer coupling with a Co-Pt layer. This coupling could be decreased by reducing the interfacial roughness in the sandwiches and the magnetisation fluctuations in each magnetic layer.

Field Emission and Atom Probe Field Ion Microscope Studies of Palladium-Silicide-Coated Silicon Emitters

R. A. KING, R. A. D. MACKENZIE, G. D. W. SMITH and N. A. CADE, *J. Vac. Sci. Technol. B*, 1995, 13, (2), 603–606
Pd-silicide-coated field emitters were prepared by Pd thermal evaporation onto Si tips, followed by annealing at 675 K. Pulsed laser atom probe analysis showed a clean near stoichiometric, Pd₂Si layer with a thin Si-enriched surface, which is converted to an oxidised layer after exposure to air. As the voltage is raised there is a large increase in field emission which corresponds to the disruption of the oxide layer.

MEDICAL USES

Platinum Anticancer Drug Binding to DNA Detected by Thickness-Shear-Mode Acoustic Wave Sensor

H. SU, P. WILLIAMS and M. THOMPSON, *Anal. Chem.*, 1995, 67, (5), 1010–1013

Nucleic acid was attached to the electrodes of thickness-shear-mode acoustic wave devices to produce a biosensor for Pt-based drugs. The decreases in series resonant frequency for interactions of DNA with both *cis*- and *trans*-platin showed two distinct kinetic processes which were explained in terms of nucleic acid binding of the hydrolysis products. Concentration-dependent decreases of series resonant frequency showed the detection limit for the drugs of ~ 10⁻⁷ M.