

# ABSTRACTS

of current literature on the platinum metals and their alloys

## PROPERTIES

### Magnetic Anisotropy of Co/Ni/Co/Pt Multilayers

P. J. H. BLOEMEN and W. J. M. DE JONGE, *J. Magn. & Magn. Mater.*, 1992, 116, (1&2), L1-L6

The magnetic anisotropy and saturation magnetisation of a series of  $30 \times (2 \text{ \AA Co} + x \text{ \AA Ni} + 2 \text{ \AA Co} + 10 \text{ \AA Pt})$  multilayers have been investigated. The easy axis of the multilayers switches from the perpendicular to along the film-plane when the thickness of the Ni  $\geq 48 \text{ \AA}$ , due to the relatively low shape anisotropy of the Ni combined with the large Co/Pt surface anisotropy.

### Microstructures of Pt-Ce and Rh-Ce Particles on Alumina and Silica

J. M. SCHWARTZ and L. D. SCHMIDT, *J. Catal.*, 1992, 138, (1), 283-293

The mechanism by which Ce promotes platinum metals catalysts is of continuing interest. Thus the effects of adding Ce to 20-200 Å diameter particles of Pt and Rh on Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> have been examined. On either substrate heating Pt in H<sub>2</sub> forms cubic particles of Pt but when Ce is also present the Pt particles no longer have square outlines. On both substrates, with Ce present Pt oxidises to Pt<sup>+2</sup> on heating in O<sub>2</sub>, and returns to PtO when heated in H<sub>2</sub>.

### Marker and Radioactive Silicon Tracer Studies of PtSi Formation

J. E. MCLEOD, M. A. E. WANDT, R. PRETORIUS and C. M. COMRIE, *J. Appl. Phys.*, 1992, 72, (6), 2232-2241

Atomic diffusion during PtSi formation was studied by marker and radioactive <sup>31</sup>Si techniques. The results showed that PtSi growth occurred either by Si substitutional diffusion or by a mixed interstitial mechanism, which is a mixture of interstitial and interstitialcy diffusion. It is suggested that Si vacancy diffusion during silicide growth is the most likely mechanism.

### Langmuir-Blodgett Films of Pt(II) Complexes. 2

H. SAMHA, T. MARTINEZ and M. K. DE ARMOND, *Langmuir*, 1992, 8, (9), 2001-2004

Two hydrophobic planar Pt(II) complexes: a charged ion pair d<sup>8</sup> complex, [bis(diphenylphosphino)ethane][5,6-dimethylphenanthroline]Pt(II) perchlorate and a neutral complex, Pt(2-(2-thienyl)-2-pyridine)<sub>2</sub>, were mixed with stearic acid and made into monolayer and multilayers Langmuir-Blodgett films. The films could be manipulated on the water surface and transferred to various substrate materials. The structures of the films were studied, and optical properties compared with solution and solid powder data.

### Infrared Absorption and Carrier Generation in Very Thin PtSi Film on p-Type Si Crystal

S. UEMATSU, *Vacuum*, 1992, 43, (11), 1039-1041

The IR absorptivity of very thin PtSi film/p-Si was examined to determine the IR absorption coefficients. The coefficients at  $\lambda = 3.0$  and  $6.0 \mu\text{m}$  depend on film thickness and increase strongly in the ultra thin region. After cooling to liquid N<sub>2</sub> temperature and on applying a low positive potential to the PtSi film, a small photocurrent was observed by IR irradiation of wavelength  $< 4.6 \mu\text{m}$ . The PtSi-Si interface has a Schottky barrier of estimated height 0.27 eV. The Schottky barrier of film  $\leq 10 \text{ nm}$  has highest IR response.

### The Chemistry of Pd in Cellulose Acetate

S.-T. HWANG and I.-W. SHIM, *J. Appl. Polymer Sci.*, 1992, 46, (4), 603-609

Pd(OAc)<sub>2</sub> has been incorporated in cellulose acetate (CA) as a dispersion medium using THF as cosolvent, giving light brown Pd-CA films with 10-20 wt.% Pd complex concentration, which are thermally stable up to 150°C. Interactions and chemical reactivities were investigated. Two different Pd carbonyls (active to H<sub>2</sub> and O<sub>2</sub>) and an active Pd(0)-hydride species formed in CA and were characterised by their IR spectra.

### Dependence of the Magnetic Properties of Co/Pd Multilayered Films on the Structural Parameters Estimated Accurately by X-Ray Diffraction

S. K. KIM, J. S. KANG, J. I. JEONG, J. H. HONG, Y. M. KOO, H. J. SHIN and Y. P. LEE, *J. Appl. Phys.*, 1992, 72, (10), 4986-4988

Studies of magnetic properties of Co/Pd multilayered films containing a few atomic layers of Co were prepared by alternating depositions in an ultrahigh-vacuum physical-vapour deposition system, and showed a dependence on Pd predeposition and Pd sublayer thicknesses as well as on Co sublayer thickness. The Pd-predeposited films had a very high coercivity of 4723 Oe and greatly enhanced interfacial magnetic anisotropy of 0.72 mJ/m<sup>2</sup>.

### Structure and Magnetic Properties of Fe/Pd Compositionally Modulated Films

L. ZHANG, Y. LIU and H. WANG, *Acta Metall. Sin.*, 1992, 28, (9), 408-412

Studies of modulation and crystal structures of Fe/Pd compositionally modulated films (CMF) prepared by vapour deposition from two sources onto a glass substrate under vacuum were performed by X-ray diffraction. The Pd layer in the Fe/Pd CMF is of f.c.c. structure and the Fe layer structure changes from b.c.c. to amorphous with decreasing Fe layer thickness.

### Induced 3D Magnetism in the Ternary Intermetallic Compound Pd<sub>2</sub>GdIn

K.-U. NEUMANN, J. CRANGLE, R. T. GILES, D. VISSER, N. K. ZAYER and K. R. A. ZIEBECK, *Solid State Commun.*, 1992, **84**, (5), 577-580

Magnetisation measurements on Pd<sub>2</sub>GdIn chemically disordered into the B2 structure showed a magnetically ordered state at < 7 K. The saturation magnetisation obtained in fields up to 5 T using a squid magnetometer yielded an extrapolated moment at 0 K significantly larger than that expected for a Gd<sup>3+</sup> ion. Above ~ 15 K the Curie-Weiss susceptibility produced an effective moment closer to that expected for Gd<sup>3+</sup>. It is suggested that the local moment on the Gd atoms polarises the Pd atoms through an indirect exchange mechanism. Below ~ 7 K there is a field-induced transition ferromagnetism.

### Electronic Properties of Ternary Hydrides A<sub>2</sub>PdH<sub>2</sub> (A = Li, Na)

R. V. KASOWSKI, D. NORÉUS, L. WANG and M.-H. WHANGBO, *Inorg. Chem.*, 1992, **31**, (23), 4737-4739

First principles pseudofunction self-consistent-field band electronic structure calculations were performed for ternary hydrides A<sub>2</sub>PdH<sub>2</sub> (A = Li, Na) to find whether these hydrides are semimetals. In previous studies of electrical resistivity measured as a function of temperature down to 4.2 K, Na<sub>2</sub>PdH<sub>2</sub> was shown to be a metal. Analysis of the Fermi surface of A<sub>2</sub>PdH<sub>2</sub> predicts that these hydrides are primarily two-dimensional metals with good conductivity in the *ab* plane.

### On New Ternary Gallides LnPd<sub>2</sub>Ga with the YPd<sub>2</sub>Si-Type Structure

F. HULLIGER, K. MATTENBERGER and S. SIEGRIST, *J. Alloys Compd.*, 1992, **190**, (1), 125-128

Crystal structure studies of the compounds LnPd<sub>2</sub>Ga (Ln = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy) indicated that they have an orthorhombic YPd<sub>2</sub>Si-type structure: an ordered variant of the Fe<sub>3</sub>C type. The compounds with Ln = Ce, Nd, Sm, Gd, Tb, Dy order magnetically with ordering temperatures of 3-24 K.

### Synthesis and Properties of Novel Ruthenium Thin-Film Materials: Self-Assembled Multilayer Approaches

D. LI, D. C. SMITH, B. I. SWANSON, J. D. FARR, M. T. PAFFETT and M. E. HAWLEY, *Chem. Mater.*, 1992, **4**, (5), 1047-1053

The synthesis and characterisation of stable Ru thin films by low temperature aqueous solution techniques where self assembled monolayers are used to enhance adhesion, are reported. A monolayer of *N*-[3-(trimethoxysilyl)propyl]ethylenediaminetriacetate was put first onto a fused SiO<sub>2</sub> surface, followed by non-electrolytic deposition of a Ru thin film using Ru(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>. The metallic mirror Ru films have typical thickness of 1500 Å, and surface morphology has 10-25 nm structural domains. The mirror films mainly contain Ru metal with 10-20 % concentration of O as the sub-oxide of RuO.

### Oxidative Dissolution of Ruthenium Dioxide Hydrate by Periodate Ions

A. MILLS and P. SAWUNYAMA, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, (17), 2487-2491

The oxidative dissolution of RuO<sub>2</sub>·xH<sub>2</sub>O to RuO<sub>4</sub> via periodate ions, IO<sub>4</sub><sup>-</sup>, has been investigated in acidic solution. The IO<sub>4</sub><sup>-</sup> appears to act as a two-electron oxidant. The kinetics fit a reaction scheme in which the rate-determining step is the reaction between a surface site and an adsorbed IO<sub>4</sub><sup>-</sup> ion, and there is competitive adsorption by any IO<sub>4</sub><sup>-</sup> present.

## CHEMICAL COMPOUNDS

### Synthesis of Palladium and Platinum Nanoclusters within Microphase-Separated Diblock Copolymers

Y. N. C. CHAN, G. S. W. CRAIG, R. R. SCHROCK and R. E. COHEN, *Chem. Mater.*, 1992, **4**, (4), 885-894

Metal nanoclusters can exhibit different chemical and physical properties to the bulk metal. Now a route has been established for the formation of Pt and Pd clusters that are < 100 Å in diameter, have a narrow size distribution and are dispersed evenly within the organometallic block of microphase-separated diblock copolymers exhibiting lamellar and cylindrical morphologies.

### Evidence of the Formation of Zerovalent Palladium from Pd(OAc)<sub>2</sub> and Triphenylphosphine

C. AMATORE, A. JUTAND and M. A. M'BARKI, *Organometallics*, 1992, **11**, (9), 3009-3013

The mixture Pd(OAc)<sub>2</sub> + *n*PPh<sub>3</sub> (*n* ≥ 2) and the complex Pd(OAc)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (1) generally used as catalysts in reactions involving aryl and vinyl halides, aryl triflates or allylic acetates spontaneously generate a zerovalent Pd complex which reacts with iodobenzene. Triphenylphosphine reduced the divalent Pd from the complex (1) by an intramolecular reaction and was oxidised to triphenylphosphine oxide. In excess triphenylphosphine, the zerovalent Pd complex generated in situ had the same <sup>31</sup>P NMR and cyclic voltammetric properties as those of Pd<sup>0</sup>(PPh<sub>3</sub>)<sub>4</sub>.

### Synthesis and Structure of a Thioazobenzene Palladacycle: Oxygen Insertion into the Pd-C Bond by *m*-Chloroperbenzoic Acid

C. K. PAL, S. CHATTOPADHYAY, C. SINHA and A. CHAKRAVORTY, *J. Organomet. Chem.*, 1992, **439**, (1), 91-99

Studies of the complex PdL<sup>1</sup>Cl prepared by the reaction of *p*-tolyl-*o'*-(2-chloroethylthio)azobenzene with Na<sub>2</sub>PdCl<sub>2</sub> showed that the azobenzene ligand acted in the tridentate (C, N, S) way with the fourth coordination position being occupied by the chloride ion. Reaction of PdL<sup>1</sup>Cl with *m*-chloroperbenzoic acid leads to insertion of O into the Pd-C bond to yield the corresponding phenolato complex. The insertion reaction is first order with respect to each reactant and has a large negative entropy of activation.

### **Bis(cymene)hexachlorotriruthenium(II)—A Novel Trinuclear Ru<sup>II</sup>-Ru<sup>II</sup>-Ru<sup>II</sup> Halide**

R. GOERISSEN, U. KOELLE and T. P. SPANIOL, *Polyhedron*, 1992, 11, (18), 2317–2320

Structural studies were performed on a new diamagnetic trinuclear linear chain complex (cymene)Ru( $\mu$ -Cl)<sub>2</sub>Ru( $\mu$ -Cl)<sub>2</sub>Ru(cymene) (1) which was prepared by irradiation of the (arene)Ru-chloro complex [Ru(cymene)Cl<sub>2</sub>]<sub>2</sub>. During cyclic voltammetry a single reversible oxidation wave was assigned to a Ru(II/III) oxidation of the central Ru atom. An anodic shift of 0.9 V of the electron transition in (1) compared to the redox potential for RuCl<sub>4</sub><sup>3+</sup>/<sup>4+</sup> was interpreted as a stabilisation of the central Ru(II) in an octahedral environment of chlorine ligands.

## **ELECTROCHEMISTRY**

### **Applicability of Reference Electrode Types in Transient Electrochemical Experiments**

S. W. WATSON and B. W. MADSEN, *Corrosion*, 1992, 48, (9), 727–733

The high impedance response of various Pt reference electrodes was tested in H<sub>2</sub>SO<sub>4</sub> solutions, specifically for IR drop compensation on current interruption. Electrodes tested were: a SCE reference, a dual electrode made of a Pt wire and a SCE connected by a 0.1  $\mu$ F capacitor, and a pseudo Pt reference. In 0.01 and 0.1 N solutions the Pt and dual electrode responded at a faster rate than the SCE. When the Pt wire from either system was put near the tip of a Luggin probe the response time was much faster; however, when the Pt wire was put in the beaker with the SCE the problem remained. The dual reference was the best overall for studying solutions of wide conductivity.

### **Behavior of Hydrazine and Its Effects on the Adsorption of Hydrogen at Pt(322) and Pt(111) Electrodes in Sulfuric Acid Solutions**

C. NISHIHARA, I. A. RASPINI, H. KONDOH, H. SHINDO, M. KAISE and H. NOZOYE, *J. Electroanal. Chem.*, 1992, 338, (1+2), 299–316

The voltammetry of Pt(322) and Pt(111) electrodes in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution was studied in the presence and absence of hydrazine. Hydrazine adsorbs on both step and terrace sites between 0.10 and 0.30 V (vs. RHE). The oxidation potential of hydrazine on step sites is 0.2 V more positive than that on terrace sites, and it adsorbs preferentially on step sites.

### **Electrocatalytic Oxidation of Methanol on Platinum Microparticles in Polypyrrole**

D. J. STRIKE, N. F. DE ROOIJ, M. KOUDELKA-HEP, M. ULMANN and J. AUGUSTYNSKI, *J. Appl. Electrochem.*, 1992, 22, (10), 922–926

The oxidation of MeOH on Au electrodes modified with polypyrrole and Pt was studied by cyclic voltammetry and by 12 h polarisation in MeOH solutions. The electrode modified with polypyrrole and Pt showed higher currents and lower rates of drift than unmodified Pt or platinised Au electrodes.

### **The Electrochemical Reaction of Sulphur-Oxygen Compounds—Part II. Voltammetric Investigation Performed on Platinum**

T. HEMMINGSEN, *Electrochim. Acta*, 1992, 37, (15), 2785–2790

The behaviours of sulphide, thiosulphate, sulphite, dithionite and sulphate anions were examined on a Pt ring at a ring-disk electrode by a triangular sweep technique. All S anions, except for sulphate, adsorb strongly on the Pt surface and prevent adsorbed H from being oxidised. This behaviour on the Pt electrode with the potential sweep method could be used analytically to determine S products and intermediates in situ and to quantify different S products.

### **On the Study of Adsorbed Species at Platinum from Methanol, Formic Acid and Reduced Carbon Dioxide via *in situ* FT-ir Spectroscopy**

T. IWASITA, F. C. NART, B. LOPEZ and W. VIELSTICH, *Electrochim. Acta*, 1992, 37, (12), 2361–2367

Three different co-ordinated forms of CO adsorbed on the Pt surface were observed for MeOH, HCOOH and reduced CO<sub>2</sub>: linear-, bridge- and multi-bonded CO. Absolute absorption bands are observed for the adsorption of MeOH and reduced CO<sub>2</sub> on using a new approach, which enables sample spectra to be computed with respect to a reference spectrum taken before adsorption. Thus the presence of a COH adsorbate is demonstrated. If Pt/Ru is used as a bifunctional catalyst for water splitting and CO/COH oxidation, surface poisoning during the oxidation of MeOH is diminished, giving I/V relationships.

### **Oxygen Isotope Exchange over a Pt Electrode in a Cell with Solid Oxide Electrolyte**

V. A. SOBYANIN, V. I. SOBOLEV, V. D. BELYAEV, A. K. DEMIN and O. A. MAR'INA, *React. Kinet. Catal. Lett.*, 1992, 47, (2), 327–332

The homomolecular O exchange over a Pt electrode in the electrochemical cell: <sup>16</sup>O<sub>2</sub> + <sup>18</sup>O<sub>2</sub>, Pt|ZrO<sub>2</sub> (10 mol.% Y<sub>2</sub>O<sub>3</sub>)|Pt, air shows that an electric current passing through the cell (a flow of O<sup>2-</sup> anions through the electrolyte) does not change the rate of exchange with respect to its open circuit value. Thus, passing electric current does not affect the bond strength of O adsorbed on the Pt electrode, and suggests that the current ideas on the nature of the NEMCA need to be amended.

### **The Preparation of a Highly Dispersed Pd+Ag/Carbon Electrocatalyst and Its Properties**

Y. YANG, Y. ZHOU, C. CHA and W. M. CARROLL, *J. Electroanal. Chem.*, 1992, 338, (1+2), 251–267

Well dispersed Pd+Ag alloy catalysts on C were prepared, giving metal particles of 2–8 nm size, in three steps: (1) functionalisation of the surface of activated C with I preadsorption, (2) the co-precipitation of Pd<sup>2+</sup> and Ag<sup>+</sup> on C and (3) the reduction of PdI<sub>2</sub> and AgI co-deposits on the C surface. Using this method bimetallic alloys can be formed at room temperature.

### Electrochemical Study of Some Palladium Compounds at a Carbon Paste Electrode—Application to the Determination of Palladium in Oxidation Automotive Catalysts

F. A. ADEKOLA, M. DIAW, C. COLIN and D. BAUER, *Electrochim. Acta*, 1992, 37, (13), 2491–2495

A carbon paste electrode was constructed and used to study the electrochemical behaviour of Pd(II), Pd(0) and Pd black. The reduction of PdO to Pd metal occurred at ~20 mV/SCE in 0.5 M HClO<sub>4</sub>, and the freshly deposited Pd metal was easier to oxidise than commercial Pd. In the new catalyst Pd was present as Pd(0), while a substantial fraction was converted into PdO in the spent catalyst.

### Methanol Oxidation on Modified Iridium Electrodes

M. S. URETA-ZAÑARTU, P. BRAVO and J. H. ZAGAL, *J. Electroanal. Chem.*, 1992, 337, (1+2), 241–251

The electro-oxidation of MeOH on clean Ir and on Ir electrodes modified by underpotential deposition and/or sub-monolayer deposits of Ag, Bi, Cd, Cu, Hg, Tl, Re and Pb, was studied in both acid and alkaline media. The catalytic effects of these atoms in acid medium decrease in the order: Pb ≈ Bi > Tl > Cd > Cu > Hg. In alkali media, the oxidation changes on the bare Ir were 16 times larger than in acid, but the metal adatoms acted as inhibitors.

### Fluxional Behaviour of [Ir<sub>4</sub>(CO)<sub>11</sub>H]<sup>-</sup> in Solution

M. J. DAVIS and R. ROULET, *Inorg. Chim. Acta*, 1992, 197, (1), 15–20

The fluxional behaviour of [Ir<sub>4</sub>(CO)<sub>11</sub>H]<sup>-</sup> was studied by <sup>13</sup>C NMR which revealed two mechanisms of similar rates at 175 K. Unlike all other Ir<sub>4</sub> carbonyl clusters studies with fluxionalities due only to CO site exchanges, the non-CO ligand participates in the lowest energy intramolecular process.

### Brine Electrolysis Using a Perfluorinated Cation-Exchange Membrane. III. Performances of Anodes for Zero-Gap Electrolysis Cells

T. MORIMOTO, T. MATSUBARA and S.-I. OHASHI, *Denki Kagaku*, 1992, 60, (7), 649–656

An anode has been developed for a zero-gap electrolysis cell, where it is contacted with a cation-exchange membrane by thin inorganic non-electrode layers on its surface and attacked by NaOH diffused through the membrane from a cathode chamber. A solid solution of RuO<sub>2</sub> and IrO<sub>2</sub> resisted corrosion from anodic polarisation in 14 wt.% NaOH solution and in brine. The performance and stability of RuO<sub>2</sub>, IrO<sub>2</sub> and TiO<sub>2</sub> anodes on a Ti substrate for the cell depend mainly on the coating composition and the heat treatment. RuO<sub>2</sub>, IrO<sub>2</sub> and TiO<sub>2</sub> coatings in molar ratio of 3:2:5 to 3:5:8 had a chlorine overvoltage of 70 mV in anolyte of pH = 3 at 90°C and 30 A/dm<sup>2</sup>. The O content in chlorine was 0.3%.

### Electrocatalytic Reduction of Nitrite at an [Os(bipy)<sub>2</sub>(PVP)<sub>10</sub>Cl]Cl-Modified Electrode

A. P. DOHERTY and J. G. VOS, *J. Chem. Soc., Faraday Trans.*, 1992, 88, (19), 2903–2907

The electrocatalytic reduction of nitrite at an electrode modified with the redox polymer [Os(bipy)<sub>2</sub>(PVP)<sub>10</sub>Cl]Cl, where bipy = 2,2'-bipyridyl, PVP = poly(4-vinylpyridine), is described. The kinetics of the mediated reaction were examined and compared to a theoretical rate equation describing the proposed mechanism. The reaction proceeded through the species NO<sup>•</sup>.

### Electrocatalysis of the Reduction of O<sub>2</sub> to H<sub>2</sub>O by Tetraruthenated Cobalt *meso*-Tetrakis(4-pyridyl)porphyrin Adsorbed on Graphite Electrodes

C. SHI and F. C. ANSON, *Inorg. Chem.*, 1992, 31, (24), 5078–5083

The co-ordination of Ru(NH<sub>3</sub>)<sub>5</sub> groups to the four pyridine sites in Co *meso*-tetrakis(4-pyridyl)porphyrin adsorbed on pyrolytic graphite electrodes resulted in complete ruthenation of the pyridine groups of the adsorbed porphyrin. The complex had good electrocatalytic activity for the reduction of O<sub>2</sub>, and the rates were higher than when it was coated in Nafion on electrodes. The catalyst is more stable in Nafion than when irreversibly adsorbed, but the higher currents obtained from the adsorbed catalyst make this immobilisation method more attractive.

### Electrocatalytic Oxidation of Benzyl Alcohol with a Monooxoruthenium(V) Complex in Solution and Inside Nafion Films

K.-Y. WONG, V. W.-W. YAM and W. W.-S. LEE, *Electrochim. Acta*, 1992, 37, (14), 2645–2650

[Ru<sup>V</sup>(L)(O)]<sup>2+</sup>, where LH = bis(2-(2-pyridyl)ethyl)(2-hydroxy-2-(2-pyridyl)ethyl)amine, is an active electrocatalyst for the electro-oxidation of benzyl alcohol in solution. When immobilised in Nafion films the activity is retained, but in aqueous acidic media the oxidation of [Ru<sup>III</sup>(L)(H<sub>2</sub>O)]<sup>2+</sup> to [Ru<sup>V</sup>(L)(O)]<sup>2+</sup> is slow in Nafion. When the pH is raised to neutral, oxidation of the complex inside Nafion becomes easier and the activity of the modified electrode for alcohol oxidation increases.

### Physico-Chemical and Electrochemical Characterization of Ru-Based Ternary Oxides Containing Ti and Ce

L. A. DE FARIÁ, J. F. C. BOODTS and S. TRASATTI, *Electrochim. Acta*, 1992, 37, (13), 2511–2518

Ce was substituted for Ti in 30 mol.% RuO<sub>2</sub> + 70 mol.% TiO<sub>2</sub>, and the effect of mixing Ru and Ce was examined. Ternary oxides of formula Ru<sub>0.3</sub>Ti<sub>1.0-0.7-x</sub>Ce<sub>x</sub>O<sub>2</sub> were formed with x = 0–0.7 at 10 mol.% intervals by thermal decomposition of aqueous acid solutions of the chlorides as precursors using Ti as a support. Electrodes were characterised in acid solution. The electrodes are much more stable in alkali than in acid, indicating anodic and cathodic inertness.

## Electrochemical Preparation and Behaviour of Poly{pyrrole-[Ru(trpy)(bpy)(OH<sub>2</sub>)]<sup>2+</sup>} (trpy = 2,2':6',2''-terpyridine) (bpy = 2, 2'-bipyridine) Films. Application to the Electrocatalytic Oxidation of Alcohols

W. F. DE GIOVANI and A. DERONZIER, *J. Electroanal. Chem.*, 1992, 337, (1+2), 285-298

The title complex has been found to exhibit the same electrochemical behaviour in weakly co-ordinating organic solvents, such as methylene chloride and acetone, as it does in water. The formation of the corresponding oxo complex [Ru(trpy)(byp)O]<sup>2+</sup> allows electrodes to be easily modified by anodic electropolymerisation of monomers containing trpy and bpy ligands substituted by a pyrrole group. In water the modified electrodes are active catalysts for alcohol oxidation, and the Ru<sup>IV</sup>=O complex is a useful oxidant in homogeneous electrocatalysis.

## PHOTOCONVERSION

### Intrazeolitic Photoinduced Redox Reactions between Ru(bpy)<sub>3</sub><sup>2+</sup> and Methylviologen

P. K. DUTTA and W. TURBEVILLE, *J. Phys. Chem.*, 1992, 96, (23), 9410-9416

The photoinduced electron transfer between Ru(bpy)<sub>3</sub><sup>2+</sup> and methylviologen in the supercages of hydrated zeolite Y was studied. The size of the Ru(bpy)<sub>3</sub><sup>2+</sup> molecules ensures it is trapped within the supercages, but it can interact with molecules in the neighbouring cages through the 7-Å ring openings. Evidence for photoelectron transfer from entrapped Ru(bpy)<sub>3</sub><sup>2+</sup> to methylviologen in neighbouring cages is given by time-resolved resonance Raman spectroscopy. Two pathways for transferring electrons were observed: rapid back electron transfer from MV<sup>•+</sup> to Ru(bpy)<sub>3</sub><sup>2+</sup> via a second-order process on the microsecond time scale and a slower process leading to charge separation and stabilisation of the redox pairs for extended periods.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Effects of Substrate Temperature, Deposition Pressure, and Thickness on the Morphology of Ultrathin Platinum Film on SiO<sub>2</sub>/Si Substrate

R. N. ESFAHANI, G. J. MACLAY and G. W. ZAJAC, *Thin Solid Films*, 1992, 219, (1-2), 257-265

The morphology of Pt film deposited by e-beam evaporation at room temperature onto SiO<sub>2</sub> was studied using the variation of its electrical resistance with its thickness. For thicknesses < 1.3 nm the Pt film is in a discontinuous island; at ~2 nm the film is very continuous electrically, but porous; while for films deposited at 250°C the morphology is island-like for thickness < 0.5 nm and continuous and porous at ~1.8 nm. As Pt deposition temperature increases the films become more uniform, but with larger grains.

## Porosity of Composite Palladium, Palladium-Nickel and Gold Electrodeposits

E. J. KUDRAK, J. A. ABYS, V. CHINCHANKAR and J. J. MAISANO, *Plat. Surf. Finish.*, 1992, 79, (2), 49-55

The porosity of connector components plated under typical manufacturing conditions including low current density were evaluated for Pd and Pd-Ni electrodeposited composites. The composite finish, known as Au-Flashed Pd (GFPd) or Au-Flashed Pd-Ni (GFPdNi) consisted of a 4.0 μm Ni sub-plate, a 0.25-2.5 μm thick Pd or Pd-Ni layer, and a flash of Co hard Au. A novel acid Pd strike process was also examined. The GFPdNi had markedly low porosity, while the acid Pd strike reduced the porosity to a nearly pore-free finish for the GFPd, even at thicknesses below 1.0 μm.

## APPARATUS AND TECHNIQUE

### A Low-Temperature Oxygen Sensor Based on the Si/LaF<sub>3</sub>/Pt Capacitive Structure

S. KRAUSE, W. MORITZ and I. GROHMANN, *Sens. Actuators B*, 1992, 9, (3), 191-196

A new O<sub>2</sub>-sensitive Si/LaF<sub>3</sub>/Pt structure working on the basis of the field effect in Si has been developed. It can detect O<sub>2</sub> both in gas mixtures and in liquid. A low 90% response time of 90 s and Nernstian sensitivity of 59 mV/lg p<sub>O<sub>2</sub></sub> were obtained. The sensor can detect O partial pressures within a range of eight orders of magnitude.

### Thin Film Permeation Membranes for Hydrogen Purification

G. MEUNIER and J. P. MANAUD, *Int. J. Hydrogen Energy*, 1992, 17, (8), 599-602

Studies of thin film Ni and Pd membranes supported by a microporous substrate made for H diffusion showed that they allow a significant increase in the permeation rate of pure H compared to that of bulk materials. The best substrates used for carrying thin film membranes were α-Al<sub>2</sub>O<sub>3</sub> tubes, and the gas-tightness was achieved by electrolytic plating. For Pd electrodeposition, a Pd tetramine sulphate bath giving good deposits without tensile stress for large thicknesses was used. It is suggested that Pd membranes ought to be used at temperatures above 300°C.

### The Influence of Technological Factors on the Hydrogen Sensitivity of MOSFET Sensors

S. FOMENKO, S. GUMENJUK, B. PODLEPETSKEY, V. CHUVASHOV and G. SAFRONKIN, *Sens. Actuators B*, 1992, 10, (1), 7-10

Integrated H<sub>2</sub> sensors based on Pd-SiO<sub>2</sub>-Si structures have been developed. The sensor Si chip consists of a test capacitor, MOSFETs, a heater and a thermosensor. Pd thin-film deposition was performed by four different methods and two contact bondings were used. The sensors with a Pd gate deposited by total Pd deposition and ion-plasma etching of Pd (C-type) showed the best rate of H response and the least relaxation time in ambient air.

### An Overview of the Ion Beam Mixing Rates in Pd/Si Bilayers versus the Temperature and Deposited Energy

J. DESIMONI, A. TRAVERSE and M.-G. MEDICI, *Nucl. Instrum. Methods Phys. Res.*, 1992, **B72**, (2), 197–201

The role of temperature and the density of energy deposited from nuclear collisions ( $F_d$ ) on the kinetics of Pd/Si ion beam mixing have been examined. The changes in mixing variance have been followed in the temperature range 80–573 K, and for nuclear collisions from 2.8 to 6.2 keV/nm. The dependence of the mixing variance on the fluence in Pd/Si bilayers shows different behaviours above and below a critical fluence. When ion beam mixing is carried out  $\geq 480$  K radiation enhanced diffusion growth takes place. Pd<sub>2</sub>Si grows under irradiation with similar activation energy to thermal annealing but with enhanced velocity constant, and is seen at high and low  $F_d$ .

### The Role of Additives in Tin Dioxide-Based Gas Sensors

H.-W. CHEONG, J.-J. CHOI, H. P. KIM, J.-M. KIM, J. KIM and G.-S. CHURN, *Sens. Actuators B*, 1992, **9**, (3), 227–231

Studies of the effect of additives PdCl<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Nb<sub>2</sub>O<sub>5</sub> in SnO<sub>2</sub> gas sensors on the gas sensing behaviour showed that the sensitivity of PdCl<sub>2</sub>-doped SnO<sub>2</sub> to both CO and CH<sub>3</sub>CN in the low-temperature region below 300°C was greatly increased. The major oxidation states of Pd in 0.5 wt.% PdCl<sub>2</sub>-doped SnO<sub>2</sub> sintered at 800°C and 650°C are 4+ and 2+, respectively. When exposed to H<sub>2</sub> at room temperature, the major oxidation state of Pd in 0.5 wt.% PdCl<sub>2</sub>-doped SnO<sub>2</sub> sintered at 800°C changed from 4+ to 2+.

### Rhenium-Osmium Isotope Ratio Determination by ICP-MS

S. B. BENETEAU and J. M. RICHARDSON, *At. Spectrosc.*, 1992, **13**, (4), 118–122

An inductively coupled plasma-mass spectroscopy may be used to determine Os and Rh isotopes in geological materials; thus sulphide mineral samples from Falconbridge East Mine yield an isochron with an age of  $1825 \pm 52$  million years and a <sup>187</sup>Os:<sup>188</sup>Os ratio of 0.54, linking this ore with the igneous silicate phase of the Sudbury Intrusive Complex.

### Luminescent pH Sensors Based on Di(2,2'-bipyridyl)(5,5'-diaminomethyl-2,2'-bipyridyl)-ruthenium(II) Complexes

R. GRIGG and W. D. J. A. NORBERT, *J. Chem. Soc., Chem. Commun.*, 1992, (18), 1300–1302

A series of luminescent pH sensors based on [Ru<sup>II</sup>(bpy)<sub>2</sub>]<sup>2+</sup> (bpy=2,2'-bipyridyl) having the acid-base sites buffered from the bipyridine ligand by a methylene spacer are reported. They display proton assisted retrieval of luminescence in R = -NMeC<sub>6</sub>H<sub>4</sub>OMe-4, etc., and proton assisted quenching of luminescence in R = -NMePh (both due to photoinduced electron transfer) and proton promoted luminescence quenching.

### Fiber-Optic Sensing of Carbon Dioxide Based on Excited-State Proton Transfer to a Luminescent Ruthenium(II) Complex

G. ORELLANA, M. C. MORENO-BONDI, E. SEGOVIA and M. D. MARAZUELA, *Anal. Chem.*, 1992, **64**, (19), 2210–2215

Luminescence quenching by proton transfer to the excited tris[2-(2-pyrazinyl)thiazole]ruthenium(II) cation has been studied, and absorption (480 nm) and emission (652 nm, 320-ns lifetime) features of the cation are discussed as a function of pH, and the nature and concentration of the buffer.

## JOINING

### Interfaces between Alumina and Platinum: Structure, Bonding and Fracture Resistance

M. DE GRAEF, B. J. DALGLEISH, M. R. TURNER and A. G. EVANS, *Acta Metall. Mater.*, 1992, **40**, Suppl., S333–S344

Diffusion bonded interfaces between Pt and sapphire or polycrystalline Al<sub>2</sub>O<sub>3</sub> were examined for structure, bonding, fracture resistance, and the effect of intervening silicate phases. The intrinsic fracture resistance of the Pt/sapphire interface is high, especially when Pt has an epitaxial orientation with respect to the sapphire. The fracture resistance is degraded by amorphous silicate phases at the interface, even when discontinuous, but is not adversely affected by crystalline silicates. The silicate phase enhances bonding.

### Formation of High Adhesive and Pure Pt Layers on TiO<sub>2</sub>

I. KONDO, T. YONEYAMA and O. TAKENAKA, *J. Vac. Sci. Technol. A*, 1992, **10**, (6), 3456–3459

Vacuum-deposited Pt films are used as sensing elements on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and TiO<sub>2</sub>, but their adhesion is not good, although this may be improved by the use of a Ti intermediate layer. The adhesion of the system Pt/(Ti)/TiO<sub>2</sub>/SiO<sub>2</sub>/Si formed by vacuum deposition has been investigated by various tests, and various analytical techniques were used to examine the system. A 10 nm layer of Ti is necessary for strong adhesion.

## HETEROGENEOUS CATALYSIS

### Structure and Catalytic Activity of Alumina Supported Platinum-Cobalt Bimetallic Catalysts. 3. Effect of Treatment on the Interface Layer

Z. ZSOLDOS and L. GUCZI, *J. Phys. Chem.*, 1992, **96**, (23), 9393–9400

The structure of the interface between metal and Al<sub>2</sub>O<sub>3</sub> in a series of Pt<sub>1-x</sub>Co<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> bimetallic samples were studied by XPS. After calcination in O<sub>2</sub> at 770 K, Pt was found in the Pt(4+) valence state as an oxide species. Subsequent treatment in H<sub>2</sub> at 770 K resulted only in a partial reduction of ionic Pt into the zero valent state. The remaining Pt found in the Pt(2+) form confirms the existence of the metal-support interaction affecting the Pt-Al<sub>2</sub>O<sub>3</sub> system.

### Effect of Platinum Surface on Activity of Bifunctional Pt/Al<sub>2</sub>O<sub>3</sub> Catalyst in Alkylimidazole Synthesis from Diamines and Carboxylic Acids

K. M. GITIS, N. I. RAEVSKAJA, A. V. ZAITSEV, V. YU. BOROVKOV, S. B. KOGAN and G. V. ISAGULYANSTS, *Izv. Akad. Nauk Rossii, Ser. Khim.*, 1992, (9), 1992-1996  
The effect of Pt surface area on the activity of Pt/Al<sub>2</sub>O<sub>3</sub> catalyst was studied during the synthesis of 2-methylimidazole from ethylenediamine and acetic acid, with a H<sub>2</sub>:ethylenediamine ratio of 4:1, at 350-400°C. The surface area of Pt in the catalyst was changed by varying the Pt contents and the preparation method. The yield of 2-methylimidazole increased with the increase of the Pt surface area.

### Effect of Pt on the Character of Reduction of Cr<sup>5+</sup> Cations in the System Pt-Cr-NTSVM and Catalytic Activity in Aromatisation of Ethane and *n*-Hexane

A. A. SLINKIN, A. V. KUCHEROV, T. V. VASINA, A. V. PREOBRAZHENSII and O. V. BRAGIN, *Kinet. Katal.*, 1992, 33, (3), 682-687  
The effect of addition of Pt into Cr-NTSVM (NTSVM contains SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 35; 0.06% Na<sub>2</sub>O) on reduction of Cr<sup>5+</sup> cation localised in zeolite channels in H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, *n*-C<sub>6</sub>H<sub>14</sub>, and on the catalytic activity during aromatisation of C<sub>2</sub>H<sub>6</sub> and *n*-C<sub>6</sub>H<sub>14</sub>, was studied spectroscopically. The results showed that changing the order of addition of Pt and Cr to NTSVM greatly affects the selectivity of the aromatisation of C<sub>2</sub>H<sub>6</sub> and *n*-C<sub>6</sub>H<sub>14</sub>. A strong promotion effect of Pt on reduction of Cr<sup>5+</sup> cation in H<sub>2</sub> and CH<sub>4</sub> is established.

### Simultaneous Removal of NO and CO over V<sub>2</sub>O<sub>5</sub>-Pt-TiO<sub>2</sub> Catalyst

T. TACHI, A. KATO, H. YAMASHITA and S. MATSUDA, *Nippon Kagaku Kaishi*, 1992, (7), 689-694  
Studies of the catalytic activity of TiO<sub>2</sub> based catalysts in NO-NH<sub>3</sub> and CO-O<sub>2</sub> reactions showed that platinum group metals supported on TiO<sub>2</sub> were very active for the removal of CO, but were less active for the removal of NO. V<sub>2</sub>O<sub>5</sub> supported on Pt/TiO<sub>2</sub> was highly active for both reactions at 250°C. However, Pt supported on V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> was highly active only for the removal of NO, indicating that the order of supporting Pt and V<sub>2</sub>O<sub>5</sub> on TiO<sub>2</sub> affects catalytic activity.

### The Chemical Anchoring of Noble Metal Amine Precursors to Silica

W. ZOU and R. D. GONZALEZ, *Catal. Today*, 1992, 15, (3-4), 443-453  
The effect of pretreatment on the dispersion of supported Pt, Pd, Ru and Rh catalysts prepared from their amine precursors in basic solutions have been studied. Pretreatment in O<sub>2</sub> prior to reduction in H<sub>2</sub> at 400°C resulted in poor dispersions for Ru and Rh, moderate dispersions for Pd and high dispersions for Pt. Pretreatments in H<sub>2</sub> gave poor dispersions for Pt and Pd and high dispersions for Ru and Rh.

### Direct Catalytic Hydrodechlorination of Toxic Organics in Wastewater

S. KOVENKLIOGLU, Z. CAO, D. SHAH, R. J. FARRAUTO and E. N. BALKO, *AIChE J.*, 1992, 38, (7), 1003-1012  
In situ hydrodechlorination of various chlorinated hydrocarbons in waste water at room temperature and atmospheric pressure was attempted in a shaker reactor, with a Pd/C catalyst. The initial rates correlated well with first-order dependence of the reactant hydrocarbon adsorbed on C, and were also independent of H<sub>2</sub> pressure. Adsorption on the C support was Langmuir type. Activation energies at different catalyst loadings varied from 29-38 MJ/mol. 1,1,2-Trichloroethane was hydrodechlorinated in aqueous solution in an autoclave reactor. Pd/C catalyst had higher activity than Pd/Al<sub>2</sub>O<sub>3</sub>.

### Activity and Infrared Studies during Carbon Monoxide Oxidation over Bimetallic Palladium-Rhodium/Silica Catalyst

P. ARAYA, J. P. BERRIOS and E. E. WOLF, *Appl. Catal. A: Gen.*, 1992, 92, (1), 17-27  
A study of the activity of bimetallic Pd-Rh catalysts supported on SiO<sub>2</sub> during the oxidation of CO by O showed that their activity depended on the method of impregnation used for both metals. Catalysts prepared by the physical mixing of the monometallic Rh and Pd catalysts showed the highest activity. This was because no alloys were formed, which leads to more linear adsorbed CO being available on Rh.

### New Montmorillonite Silylpropylethylenediamine Palladium(II) Complex in Oxidation of Terminal Olefins

Y. V. SUBBA RAO, S. S. RANI and B. M. CHOUDARY, *J. Mol. Catal.*, 1992, 75, (2), 141-146  
The selective oxidation of terminal olefins to methyl ketones in quantitative yields occurs on using a heterogenised montmorillonite silylpropylethylenediamine Pd(II) complex and H<sub>2</sub>O<sub>2</sub> as reoxidant. This catalyst displays a tenfold increase in activity compared to its homogeneous counterpart, due to the change in environment from the bidentate ethylenediamine ligand and the acidity of the support under identical conditions. The catalyst has consistent activity for 4 recycles.

### Palladium-Catalyzed Norbornene-Carbon Monoxide Co-oligomerization Initiated by Aryl Groups and Terminated by Double Bond Formation

E. DALCANALE, Z. AN, L. P. BATTAGLIA, M. CATELLANI and G. P. CHIUSOLI, *J. Organomet. Chem.*, 1992, 437, (3), 375-388  
The use of *m*-iodophenol as initiator in Pd catalysed norbornene-CO oligomerisation in the presence of K acetate unexpectedly leads to termination by double bond formation in spite of the limitations to β-H-anti elimination. The presence of *endo* products points to preliminary *exo*-to-*endo* isomerisation through enolisation.

## Formation and Physico-Chemical Properties of the System PdO/ZrO<sub>2</sub>

L. S. KRAVCHUK, E. I. STEL'MAK, N. L. IVASHCHENKO, S. V. VALIEVA and V. S. MOLOD'YANOVA, *Kinet. Katal.*, 1992, 33, (3), 672-677

Physico-chemical properties of PdO/ZrO<sub>2</sub> were studied on samples prepared by co-precipitation of Pd and Zr hydroxides or by impregnation of Zr oxide from an aqueous solution of Pd nitrate with subsequent calcination at 320-900°C. Pd<sup>2+</sup> ions were found to stabilise tetragonal modification of ZrO<sub>2</sub>. An increase in reduction temperature of Pd-ZrO samples at 500-700°C was accompanied by a decrease in their H adsorption properties. Catalysts prepared by co-precipitation of PdO/ZrO<sub>2</sub> exhibited higher activity in CO than those prepared by impregnation.

## Reduction of Nitrates by Dihydrogen in CeO<sub>2</sub> and Rh/CeO<sub>2</sub> Catalysts

J. BARBIER, F. MARSOLLIER and D. DUPREZ, *Appl. Catal. A: Gen.*, 1992, 90, (1), 11-23

A series of NO<sub>3</sub><sup>-</sup>/CeO<sub>2</sub> (I) and Rh/NO<sub>3</sub><sup>-</sup>/CeO<sub>2</sub> (II) catalysts were prepared with variable loadings of nitrate (0-1.5 wt.%) and Rh (0-0.2 wt.%), and characterised. In (I) supports, the nitrate reduced into N<sub>2</sub> at 460-480°C, while the ceria reduced in a narrow peak at 530°C (surface) and a large peak above 600°C (bulk). The Rh significantly increased the reducibility of all the surface species: nitrates and the CeO<sub>2</sub> surface were reduced at the same time as the metal in a single peak at 220°C. However, nitrates retarded the reduction of Rh/CeO<sub>2</sub>, which gave a single peak at 285°C with no NaNO<sub>3</sub> present.

## Hydrogenolysis of *n*-Butane on Low-Loaded Rh/TiO<sub>2</sub>. II. Catalysts Obtained by Impregnation

M. J. HOLGADO, A. C. IÑIGO and V. RIVES, *React. Kinet. Catal. Lett.*, 1992, 47, (2), 233-238

The activity in *n*-butane hydrogenolysis of 0.6 wt.% Rh/TiO<sub>2</sub> catalysts prepared by impregnation and reduced at different heating rates is reported. The catalyst reduced at 5 K/min is ten times more active than that reduced at 20 K/min.

## The Impact of Surface Organometallic Chemistry in Heterogeneous Catalysis: A New Class of Highly Chemoselective Hydrogenation Catalysts, Rh<sub>2</sub>Sn(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>/SiO<sub>2</sub>

B. DIDILLON, J. P. CANDY, A. EL MANSOUR, C. HOUTMANN and J.-M. BASSET, *J. Mol. Catal.*, 1992, 74, (1-3), 43-49

A new generation of catalysts with organometallic fragments supported and stabilised on the surface of Rh particles: bi-metallic Rh<sub>2</sub>Sn(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>/SiO<sub>2</sub>, can be obtained by partial hydrogenolysis at 423 K of Sn(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub> on surface Rh atoms (Rh) of Rh(0) particles on SiO<sub>2</sub>. The catalyst is extremely active and selective for hydrogenating citral to the corresponding unsaturated alcohols with 96% selectivity at 100% conversion. This selectivity is observed when the Rh particles are covered with Sn(C<sub>4</sub>H<sub>9</sub>)<sub>2</sub> fragments.

## Preparation and Activities of Iridium Catalysts Supported on Thermostable Sol-Gel Alumina for the Decomposition of Hydrazine

K. MASUDA, S. MIYAZAKI, T. SANO, F. MIZUKAMI and K. KUNO, *Nippon Kagaku Kaishi*, 1992, (9), 910-914

A number of Ir/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared for the decomposition of hydrazine by using the thermostable Al<sub>2</sub>O<sub>3</sub> synthesised by an improved sol gel method. The thermal stability of the catalysts before and after thermal treatments at high temperatures in an inert gas was evaluated. The performance of Ir/Al<sub>2</sub>O<sub>3</sub> catalysts with the thermostable Al<sub>2</sub>O<sub>3</sub> was superior to that of the Ir/Al<sub>2</sub>O<sub>3</sub> catalysts using commercial Al<sub>2</sub>O<sub>3</sub>. The performance and deterioration of the Ir/Al<sub>2</sub>O<sub>3</sub> catalyst strongly depended on the solvents used during impregnation; C<sub>2</sub>H<sub>5</sub>OH was more suitable for catalyst preparation than CH<sub>3</sub>CN and H<sub>2</sub>O.

## Supercritical Phase Fischer-Tropsch Synthesis: Catalyst Pore-Size Effect

LI FAN, K. YOKOTA and K. FUJIMOTO, *AIChE J.*, 1992, 38, (10), 1639-1648

Ru/Al<sub>2</sub>O<sub>3</sub> catalysts on tailored supports with a range of pore sizes were prepared and examined for their catalytic activity and product distribution during the transfer of reactants and products in the supercritical-phase Fischer-Tropsch synthesis. With larger pore catalysts waxy products could be extracted *in situ*, while the hydrogenation or hydrocracking of olefins was suppressed. Desorption and diffusion of the product were so well balanced that the overall mass transfer of the products was most effective in the supercritical phase.

## Structure Sensitive Nitrogen Chemisorption on Supported Ruthenium Catalysts

S. K. MASTHAN, K. S. RAMA RAO, P. S. S. PRASAD and P. KANTA RAO, *Indian J. Chem.*, 1992, 31A, (7), 436-438

Dissociative N<sub>2</sub> chemisorption is the rate determining step in ammonia synthesis, and a study has been made of the influence of temperature (250-400°C) and structure of promoted and unpromoted Ru/C covered Al<sub>2</sub>O<sub>3</sub> (CCA), Cs-Ru/CCA and Cs-Ru-Ba/CCA catalysts on the nature of N<sub>2</sub> chemisorption.

## HOMOGENEOUS CATALYSIS

### The Reaction of Isoprene with Aniline on the Palladium Complex Catalyst

E. A. PETRUSHKINA and L. I. ZAKHARKIN, *Izv. Akad. Nauk Rossii, Ser. Khim.*, 1992, (8), 1794-1798

Studies of the reaction of isoprene with aniline in the presence of Pd(acac)<sub>2</sub>-Ph<sub>3</sub>P system yielded a mixture of isomeric telomers: N-(dimethyloctadien-2,7-yl-1) anilines and N-(dimethyloctadien-1,7-yl-3) anilines, while in the catalytic system Pd(acac)<sub>2</sub>-Ph<sub>3</sub>P-CF<sub>3</sub>COOH a mixture of adducts: N-(methylbuten-2-yl)anilines was formed. The reaction of N-methyl-aniline with isoprene in the system Pd(acac)<sub>2</sub>-Ph<sub>3</sub>P-CF<sub>3</sub>COOH also gave a mixture of N-methyl, N-(methylbuten-2-yl)anilines.



### **Palladium-Catalyzed Cross-Coupling Reactions in a Homogeneous Aqueous Medium**

J. P. GENET, E. BLART and M. SAVIGNAC, *Synlett*, 1992, (9), 715-717

A Pd(0) H<sub>2</sub>O-soluble catalyst Pd(AcO)<sub>2</sub>, which was prepared in situ from Pd(II) acetate-trisodium 3,3',3''-phosphinetriyltribenzenesulphonate, was found to be an efficient catalyst for various cross-coupling reactions. Examples of the coupling in this aqueous media include: inter- and intramolecular Heck reactions (acyclic and cyclic alkenes), terminal alkynes, phenyl boronic acid with iodoaromatic compounds or vinyl halide, allylic substitution with carbonucleophiles, etc.

### **Preparation of Ethyl Arylpropiolates from Aryl Iodides by Palladium-Catalyzed Cross-Coupling Reaction**

T. SAKAMOTO, F. SHIGA, A. YASUHARA, D. UCHIYAMA, Y. KONDO and H. YAMANAKA, *Synthesis*, 1992, (8), 746-748

The cross-coupling reaction of aryl iodides with 3,3,3-triethoxy-1-propyne catalysed by (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub> complex gave 1-aryl-3,3,3-triethoxy-1-propynes which were converted to the corresponding ethyl arylpropiolates. The arylpropiolates were also synthesised from the cross-coupling reactions of aryl iodides with 2-ethoxycarbonyl-1-ethynylzinc chloride or ethyl (tributylstannyl)propiolate, but the reactions were not easily applicable.

### **Palladium Catalysed Electrosynthesis Using Aryl Trifluoromethanesulfonates (Triflates). Synthesis of Biaryls and Aromatic Carboxylic Acids**

A. JUTAND, S. NÉGRI and A. MOSLEH, *J. Chem. Soc., Chem. Commun.*, 1992, (23), 1729-1730

The Pd complex [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] catalyses the electrosynthesis of biaryls from aryl triflates, while in the presence of CO<sub>2</sub> it catalyses the electrosynthesis of aromatic carboxylic acids. The electrosyntheses of the aromatic carboxylic acids and biaryls were performed under the same conditions, but in the presence of bubbling CO<sub>2</sub> carboxylic acids were formed.

### **Complexes of PdCl<sub>2</sub> with Phosphoryl and Thiophosphoryl Substituted Phosphines in the Catalysis of Olefins Hydrocarboxylation**

M. I. TEREKHOVA, T. E. KRON, N. A. BONDARENKO, E. S. PETROV and E. N. TSVETKOV, *Izv. Akad. Nauk Rossii, Ser. Khim.*, 1992, (9), 2003-2007

Studies of the effect of Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>m</sub>P(X)Ph<sub>2</sub>(L) ligands (where m = 1.2, X = 0.5) on the velocity and regioselectivity were performed during the α-olefins hydrocarboxylation reaction in the presence of PdCl<sub>2</sub> catalyst in various organic solvents. When L has m = 2 and X = 0, the high regioselectivity of > 80% was achieved, which was calculated relative to products of normal structure. The effect of type of ligand used and triphenylphosphine on the properties of the catalytic system in this reaction are compared.

### **Synthesis of Allylic Aryl Ethers via Palladium(0)-Catalyzed Arylation of Allylic Carbonates**

C. GOUX, P. LHOSTE and D. SINOU, *Synlett*, 1992, (9), 725-727

A simple route for the synthesis of allylic aryl ethers, very valuable in organic chemistry, is described. This involves the Pd(0)-catalysed O-alkylation of allylic carbonates by certain phenols.

### **New Strategies for the Synthesis of Vitamin D Metabolites via Pd-Catalyzed Reactions**

B. M. TROST, J. DUMAS and M. VILLA, *J. Am. Chem. Soc.*, 1992, 114, (25), 9836-9845

Vitamin D metabolites and analogues are important because of clinical prospects, and new Pd-catalysed reactions offer insights into their construction. Alkylative cyclisation provides a simple strategy for creating the requisite triene and also the A ring of vitamin Ds from an enyne. A catalyst produced from (dba)<sub>2</sub>Pd<sub>2</sub>CHCl<sub>2</sub> and triphenylphosphine facilitates the syntheses of alphacalcidol and calcitriol.

### **A Useful Palladium Catalyst for Addition of Ge-Ge Bonds to Alkynes**

K. MOCHIDA, C. HODOTA, H. YAMASHITA and M. TANAKA, *Chem. Lett. Jpn.*, 1992, (9), 1635-1638

The insertion of alkynes into Ge-Ge bonds of digermanes, octamethyltrigermane and decamethyltrigermane has been achieved for the first time. A Pd(dba)<sub>2</sub>-2P(OCH<sub>2</sub>)<sub>2</sub>CEt catalyst, where dba = dibenzylideneacetone, was used, typically at 120°C for 5 h, yielding the best results for the insertion of phenylacetylene.

### **Palladium Catalyzed Cross Coupling Reaction of α-Allenyl Acetates under Nonbasic Conditions**

Z. NI and A. PADWA, *Synlett*, 1992, (11), 869-870

A number of 2-thiophenyl substituted 1,3-dienes were synthesised via a Pd catalysed cross coupling reaction of α-allenyl acetates with various terminal alkynes under non-basic conditions. A mixture of allenyl acetate of the appropriate alkyne and a catalytic amount of Pd(PPh<sub>3</sub>)<sub>4</sub> in THF was heated at reflux for 30 min. Purification of the residue by flash chromatography on SiO<sub>2</sub> gel gave the corresponding diene in moderate to good yield.

### **New Homogeneous Rhodium Catalysts for the Regioselective Hydroboration of Alkenes**

S. A. WESTCOTT, H. P. BLOM, T. B. MARDER and R. T. BAKER, *J. Am. Chem. Soc.*, 1992, 114, (23), 8863-8869

Hydroboration of vinylarenes with catecholborane using [Rh(η<sup>3</sup>-2-Me-allyl){(Pr<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>}] as catalyst precursor had excellent activity and regioselectivity (>99 %) for the corresponding internal boronate ester. The catalyst gives excellent selectivity for both aryl- and aliphatic alkenes and accommodates sterically demanding alkenes without hydrogenation or isomerisation.

### Synthesis of Polyphenylacetylene Free-Standing Films in the Presence of Rhodium-Imidazole Catalysts

M. V. RUSSO, F. IUCCI, A. FURLANI, A. CAMUS and N. MARSICH, *Appl. Organomet. Chem.*, 1992, 6, (6), 517-524

Studies of a new dinuclear Rh(I) complex  $[\text{Rh}_2(\text{cod})_2(\text{imH})_2\text{im}]\text{PF}_6$  (imH = imidazole) showed that it has high catalytic activity towards the polymerisation of phenylacetylene compared to other Rh imidazole complexes. However, the complex was unstable in solution where it underwent modification leading to insoluble oligomers.

### Hydrogenation and Hydrosilylation Activity of Homogeneous and Immobilized Dicarbonyl(2,4-Pentanedionato)Rhodium Complexes

M. ČAPKA, M. CZAKOOVÁ, W. URBANIAK and U. SCHUBERT, *J. Mol. Catal.*, 1992, 74, (1-3), 335-344  
A series of homogeneous complexes of  $\text{R-C}(\text{COCH}_3)_2\text{Rh}(\text{CO})_2$ , where  $\text{R} = \text{H}$ ,  $n\text{-C}_3\text{H}_7$ ,  $(\text{CH}_3)_2\text{Si}(\text{CH}_3)$ , and  $(\text{C}_2\text{H}_5\text{O})_2\text{Si}(\text{CH}_3)$ , was prepared, and immobilised analogues were synthesised by 5 different techniques. The homogeneous complexes and the immobilised analogues are efficient catalysts for hydrogenation and hydrosilylation of alkenes; they are not sensitive to O, and immobilising the homogeneous complexes on a  $\text{SiO}_2$  surface resulted in an almost threefold increase in catalytic activity.

### Catalytic Asymmetric Synthesis with Trans-Chelating Chiral Diphosphine Ligand TRAP: Rhodium-Catalysed Asymmetric Michael Addition of $\alpha$ -Cyano Carboxylates

M. SAWAMURA, H. HAMASHIMA and Y. ITO, *J. Am. Chem. Soc.*, 1992, 114, (21), 8295-8296

A trans-chelating chiral diphosphine ligand, 2,2"-bis[1-(diphenylphosphino)ethyl]-1,1"-biferrocene (TRAP) was successfully applied to transition metal catalysed asymmetric synthesis using a Rh complex prepared in situ from  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$  and TRAP (0.1-1 mol %). The complex was an effective catalyst for asymmetric Michael addition of  $\alpha$ -cyano carboxylates with vinyl ketones or acrolein. Enantioselectivities ranging from 83-89% were obtained for the reaction. Excellent catalyst turnover efficiency for the reaction with acrolein was shown.

### Rhodium-Catalysed, Carbon Dioxide-Mediated Aerobic Oxidation of Ethers

A. K. FAZLUR-RAHMAN, J.-C. TSAI and K. M. NICHOLAS, *J. Chem. Soc., Chem. Commun.*, 1992, (18), 1334-1335

Studies of  $[\text{Rh}(\text{NBD})(\text{PMe}_2\text{Ph})_3][\text{BF}_4]$ , where NBD = 2,5-norbornadiene, complex showed that in the presence of  $\text{CO}_2$  it catalyses the aerobic oxidation of ethers to esters with co-production of formic acid. The origin of the  $\text{CO}_2$ -mediating effect could result from the involvement of a  $\text{CO}_2$ -derived transitory auxiliary ligand, such as formate or peroxocarbonate.

### Highly Selective Insertion into Aromatic C-H Bonds in Rhodium(II) Triphenylacetate-Catalysed Decomposition of $\alpha$ -Diazocarbonyl Compounds

S.-I. HASHIMOTO, N. WATANABE and S. IKEGAMI, *J. Chem. Soc., Chem. Commun.*, 1992, (20), 1508-1510  
Studies of Rh(II) triphenylacetate catalyst, which contains a bulky bridging ligand, showed an exceptionally high order of selectivity for aromatic C-H insertion over aliphatic C-H insertion or cyclopropanation in decompositions of  $\alpha$ -diazocarbonyl compounds.

## FUEL CELLS

### Hydrogen-Air Fuel Cells of the Alkaline Matrix Type: Manufacture and Impregnation of Electrodes

D. STASCHEWSKI, *Int. J. Hydrogen Energy*, 1992, 17, (8), 643-649

Development of matrix fuel cells is reported using electrodes with various collectors, PTFE bonding and Pt concentrations of the Pt/C catalyst. The electrodes have been manufactured and tested in terms of modified parameters. Parallel to the matrix cell fabrication a study of alternative vehicular propulsion has also been carried out in practice by driving an electric truck equipped with commercial alkaline fuel cell aggregates and fuelled by  $\text{H}_2$  and pure  $\text{O}_2$  gas.

### The Influence of Pt on the Electrooxidation Behaviour of Carbon in Phosphoric Acid

E. PASSALACQUA, P. L. ANTONUCCI, M. VIVALDI, A. PATTI, V. ANTONUCCI, N. GIORDANO and K. KINOSHITA, *Electrochim. Acta*, 1992, 37, (15), 2725-2730

The electro-oxidation behaviour of Pt/C catalysts for phosphoric acid fuel cells was investigated potentiostatically in the potential range 0.6-1.0 V RHE in concentrated  $\text{H}_3\text{PO}_4$  at 160°C. The corrosion rate increased with increasing Pt content and was most noticeable at 0.6 V. The surface area of Pt did not significantly change during the experiments, but the Pt content of the electrocatalyst altered dramatically due to Pt dissolution at higher potentials; at these potentials there is no metal to catalyse the corrosion of C.

### Amorphous Nickel-Valve Metal-Platinum Group Metal Alloy Electrodes for Hydrogen-Oxygen Sulphuric Acid Fuel Cells

Y. HAYAKAWA, A. KAWASHIMA, H. HABAZAKI, K. ASAMI and K. HASHIMOTO, *J. Appl. Electrochem.*, 1992, 22, (11), 1017-1024

Porous gas-diffusion electrodes prepared from alloy catalyst powders made by immersion of amorphous Ni-40Zr and Ni-40Ti alloys containing a few at. % of platinum group metals in HF solution, were used in the electrochemical reduction of O and oxidation of H in 1 M  $\text{H}_2\text{SO}_4$  at 25°C. The activity of the electrodes made from the amorphous alloys containing Pt-Ru, Pt-Rh, Pt and Pd for O reduction was much higher than that of the Pt black electrode.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Palladium Thin-Film Resistors for Josephson LSI Circuits

H. NAKAGAWA, M. AOYAGI, I. KUROSAWA and S. TAKADA, *Jpn. J. Appl. Phys.*, 1992, 31, (8), 2550–2553

Pd thin film resistors have been fabricated and investigated for reliability in Josephson LSI circuits by changing the deposition rate produced by electron-gun evaporation, the substrate insulating films, etc. Former large variations in the sheet resistance of  $\pm 15\%$  can be attributed to fluctuations in the deposition rate. Sheet resistances from 0.5–11  $\Omega$  were obtained by reducing the film thickness from 100 to 17 nm, and the reproducibility was improved to  $< \pm 2\%$ .

### Current Transport in Pd/n-InP Diodes Formed at Room and Low Temperature

Z. Q. SHI and W. A. ANDERSON, *J. Appl. Phys.*, 1992, 72, (8), 3803–3807

Ultrahigh barrier height ( $\phi_b = 0.96$  eV) Schottky diodes were obtained by depositing Pd on an n-InP substrate cooled to low temperature (LT = 77 K) with a vacuum of  $10^{-7}$  Torr. This indicated an 0.4 to 0.5 eV increase in  $\phi_b$  compared with the room temperature (RT = 300 K) deposition. The conduction mechanism was controlled by thermionic emission. For the LT diode, the value of the reverse saturation current density was about six orders smaller than for the RT diode at the same temperature.

### An Initial Investigation of the Microstructure of Ti/Pd/Au Ohmic Contact Structures for GaAs Microwave Devices Applications

B. M. HENRY, A. E. STATON-BEVAN, V. K. M. SHARMA, M. A. CROUCH and S. S. GILL, *J. Electron. Mater.*, 1992, 21, (9), 929–933

An investigation of as-deposited and annealed 75 nm Ti/75 nm Pd/400 nm Au ohmic contacts to Zn doped thin  $p^+$ -GaAs layers was performed. The annealed contacts had limited interaction between the metallisation and the semiconductor with a metal penetration depth of only 2 nm for a 4 min anneal at 380°C. The contacts were still layered after annealing and consisted of large  $\alpha$  Au(Ga) grains, a central, non-uniform layer containing small Pd-rich grains, and a lower uniform layer of almost pure Ti.

### Metallurgical Properties and Characteristics of the Pd/Zn/Pd to p-Type GaP Ohmic Contact Interface Layers

F. ZHANG, Z. SONG and J. PENG, *Appl. Surf. Sci.*, 1992, 62, (1/2), 83–88

Good ohmic contact to  $p$ -type GaP was obtained when a Pd/Zn/Pd multilayer and suitable alloying temperature were used. The metallurgical properties and characteristics of the contact layer were determined. For a hole concentration in the  $p$ -type GaP of  $2 \times 10^{17}/\text{cm}^3$ , a specific contact resistance of  $6 \times 10^{-5} \Omega/\text{cm}^2$  was obtained, during alloying at 550°C.

### Optical Bandgaps and Electron Affinities of Semiconducting Rh<sub>2</sub>O<sub>3</sub>(I) and Rh<sub>2</sub>O<sub>3</sub>(III)

F. P. KOFFYBERG, *J. Phys. Chem. Solids*, 1992, 53, (10), 1285–1288

Rh<sub>2</sub>O<sub>3</sub> (I) and Rh<sub>2</sub>O<sub>3</sub> (III) are  $p$ -type semiconductors with a hole mobility of  $< 4 \times 10^{-3} \text{ m}^2/\text{Vs}$ . Photoelectrochemical measurements showed that the valence band edges were 5.0–5.1 eV below the vacuum level and electron affinities were 3.6 eV for Rh<sub>2</sub>O<sub>3</sub> and 3.9 eV for Rh<sub>2</sub>O<sub>3</sub>(III). For both materials the optical transitions across the bandgap were indirect allowed with bandgaps of 1.41 eV for Rh<sub>2</sub>O<sub>3</sub>(I) and 1.20 eV for Rh<sub>2</sub>O<sub>3</sub>(III).

## MEDICAL USES

### Synthesis and DNA-Binding Properties of a Cisplatin Analogue Containing a Tethered Dansyl Group

J. F. HARTWIG, P. M. PIL and S. J. LIPPARD, *J. Am. Chem. Soc.*, 1992, 114, (21), 8292–8293

The synthesis, fluorescence and DNA-binding properties of a structural analogue of the anti-tumor drug cisplatin, [Pt(dansyl)Cl<sub>2</sub>], is reported. The complex binds covalently to DNA to form bifunctional 1,2-intrastrand cross-links, adducts that display analogous structures to those formed upon binding cisplatin to duplex DNA. The luminescence, cellular uptake and DNA-binding properties of this Pt complex, which contains a tethered dansyl group, should ensure several applications, such as its intracellular distribution and processing by DNA repair enzymes.

### Synthesis Characterisation and Anti-Tumour Activity of Pd-Rhodamine B Complex

L. WANG, J. WU, Z. PENG, Z. YANG and G. CHENG, *Precious Met. (China)*, 1992, 13, (2), 46–50

Pd-rhodamine B complex has been prepared and characterised, and its effect on inhibiting the growth of Hep and Ec carcinogen cells is discussed. The complex has no effect on mouse weight with Hep or Ec cancer.

### Design of a Hybrid of Two $\alpha$ -Helix Peptides and Ruthenium Trisbipyridine Complex for Photo-Induced Electron Transfer System in Bilayer Membrane

H. MIHARA, N. NISHINO, R. HASEGAWA, T. FUJIMOTO, S. USUI, H. ISHIDA and K. OHKUBO, *Chem. Lett. Jpn.*, 1992, (9), 1813–1816

A transmembrane molecular device has been designed to provide a photo-induced electron path. Two strands of an amphiphilic  $\alpha$ -helical 22-peptide were anchored on Ru trisbipyridine complex. This hybrid has the Ru complex, anthraquinone, together with viologen as photo-induced electron transfer system embedded in the bilayer membrane, and allows electron transfer reactions across the lipid layer. The design of the polypeptide system combined with photochemical studies allows efficient electron transfer systems in artificial proteins to be constructed.