

# ABSTRACTS

of current literature on the platinum metals and their alloys

## PROPERTIES

### The Stabilization of Formate on Pt(111) by Coadsorbed Atomic Oxygen

M. R. COLUMBIA and P. A. THIEL, *Chem. Phys. Lett.*, 1994, **220**, (3,4,5), 167-171

The stabilisation of adsorbed formate, by coadsorbed atomic oxygen, on Pt(111) was examined spectroscopically, and the stability increased in two ways: the conversion temperatures of formic acid to formate, and then formate to gaseous CO, are lower and higher, respectively, than in the absence of O. The saturation yields of the dehydrogenation products were ~ 5 times greater than those produced on a clean surface. This effect is linked to an increase in the initial sticking coefficient of the formic acid.

### An Investigation of Component Interaction in the Yb-Pt-Ge System

O. L. BORISENKO, O. I. BODAK and YU. D. SEROPEGIN, *Vestn. Mosk. Univ., Ser. Khim.*, 1994, **35**, (1), 106-109  
Studies of phase equilibria in the Yb-Pt-Ge system have been performed and the isothermal section of the phase diagram was plotted showing the state of Yb-Pt-Ge at 870 K. The diagrams indicated the presence of three new ternary intermetallic compounds: Yb<sub>2</sub>PtGe, of type Ce<sub>2</sub>CuGe, with a = 0.3949, b = 0.4247 and c = 1.975 nm; YbPtGe, of type YIrGe, with a = 0.4337, b = 0.8734 and c = 1.6134 nm; and YbPtGe of type TiNiSi with a = 0.6897, b = 0.4325 and c = 0.7542 nm.

### Isothermal Section of the Phase Diagram of the Pt-Rh-W System at 1100°C

T. G. MURZAGEREEV, M. V. RAEVSKAYA, G. P. ZHMURKO, K. B. KALMYKOV and V. K. PORTNOI, *Vestn. Mosk. Univ., Ser. Khim.*, 1994, **35**, (1), 93-97

Phase equilibrium in the Pt-Rh-W system at 1100°C was measured by physico-chemical analysis, and diffusion vapour techniques. The hexagonal ε-phase formed in Rh-W system, and penetrated into the ternary Pt-Rh-W which contained ≤ 40 at.% Pt.

### High-Temperature Diffusion of Hydrogen and Deuterium in Palladium

T. MAEDA, S. NAITO, M. YAMAMOTO, M. MABUCHI and T. HASHINO, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, (6), 899-903

Studies of the diffusivity and solubility of H and D in Pd measured at 773-1373 K and at H and D concentrations with atomic ratios of < 10<sup>-4</sup> H: Pd and D: Pd showed Arrhenius behaviour for the measured diffusion coefficients for H and D. A model of the diffusion in which the H atom can jump from one octahedral site into the adjacent octahedral site assisted by local deformation of the Pd lattice is described.

### Phase Separation in Amorphous Pd-17at%Si-5at%Cu

T. ABE, *Appl. Surf. Sci.*, 1994, **76/77**, 226-232

The devitrification process in Pd<sub>83</sub>Si<sub>7</sub>Cu, amorphous alloys was studied by atom-probe FIM. The amorphous state crystallised to form a super-saturated f.c.c. phase at 648 K. Particles of metastable Pd<sub>3</sub>Si (Cu) were observed after annealing for 10 min at 693 K. Additionally, metastable Pd<sub>3</sub>Cu (Si) was formed after annealing for 10 min at 743 K. The amorphous state in this alloy is more stable than the one in binary Pd-Si amorphous alloys.

### Effect of Hydrogen Absorption on Structure, Superconductivity, Magnetic Susceptibility and Heat Capacity of Zr<sub>2</sub>Rh

P. RAJ, P. SURYANARAYANA, A. SATHYAMOORTHY, K. SHASHIKALA, R. M. IYER, S. K. DHAR, L. C. GUPTA, V. C. SAHNI and R. J. BEGUM, *J. Alloys Compd.*, 1994, **206**, (1), 47-54

The superconducting intermetallic compound Zr<sub>2</sub>Rh can be hydrided at room temperature and H<sub>2</sub> pressure of ~ 1-2 atm to give compositions Zr<sub>2</sub>RhH<sub>x</sub> where x = 4.25 ± 0.25, without a change in the crystal structure. This is stabilisation of a hydride phase with an appreciable H content. Zr<sub>2</sub>RhH<sub>4.25</sub> has metallic behaviour similar to Zr<sub>2</sub>Rh, but shows no superconductivity down to 1.8 K, the hydride is Pauli paramagnetic, its Debye temperature is almost twice than of Zr<sub>2</sub>Rh and the electronic specific heat coefficient is reduced.

### High-Temperature Oxidation Behavior of Iridium-Based Alumina-Forming Ternary Intermetallics

K. N. LEE and W. L. WORRELL, *Oxid. Met.*, 1994, **41**, (1/2), 37-63

The addition of up to 20 at.% Si to the Ir-Al binary alloys reduced the Al concentration needed for the formation of a protective Al<sub>2</sub>O<sub>3</sub> scale from ≥ 55 at.% without Si to ~ 20 at.% with 20 at.% Si. Ternary Ir-Al-Si alloys containing 30-50 at.% Al and 8-10 at.% Si which were oxidised at 1 atm O<sub>2</sub> at 1550-1600°C, exhibited parabolic oxidation behaviour. Thermal cycling of the Ir-50Al-8Si and Ir-60Al samples did not result in scale spallation due to the match in coefficients of thermal expansion between the Al<sub>2</sub>O<sub>3</sub> scale and the intermetallic substrate.

### Preparation of Ultrafine IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> Binary Oxide Particles by a Sol-Gel Process

Y. MURAKAMI, S. TSUCHIYA, K. YAHIKOZAWA and Y. TAKASU, *Electrochim. Acta*, 1994, **39**, (5), 651-654

Ultrafine Ir-Ta binary oxide particles were prepared by a sol-gel method by hydrolysis and condensation of metal alkoxides in the liquid phase. The binary oxides calcined at 500°C had IrO<sub>2</sub> rutile-type phase and Ta<sub>2</sub>O<sub>5</sub> amorphous phase, while Ir oxide contained both IrO<sub>2</sub> rutile-type phase and Ir metallic phase.

## The Constitution of the Ruthenium-Tellurium System

S. BERNATH, H. KLEYKAMP and W. SMYKATZ-KLOSS, *J. Nucl. Mater.*, 1994, **209**, (2), 128–131

Studies of the constitution of the Ru-Te system in the concentration range 0–70 at. % Te at 400–1200°C showed the presence of only one intermediate compound, RuTe<sub>3</sub>, in the system, which crystallises in the metastable marcasite type at low temperatures and in the pyrite type at high temperatures. The transition is monotropic at ~470°C in equilibrium with Ru, and below 440°C in equilibrium with Te. RuTe<sub>3</sub> is hyperstoichiometric and has a narrow homogeneity region at 67.3–67.8 at. % Te. The compound decomposes at 1175°C and 1 bar into Ru and gaseous Te. The maximum Te solubility in Ru is 0.13 at. % Te at 1000°C.

## CHEMICAL COMPOUNDS

### Reactions of Thermal, Photolytic and Oxidative Transformation of Homoligand Carbonyls of Group VI-VIII Metals

I. V. SPIRINA and V. P. MASLENNIKOV, *Usp. Khim.*, 1994, **63**, (1), 43–56

A review is given of the mechanisms of thermal, photochemical and oxidative transformations of metal carbonyls to highly dispersed metallic and oxide phases. The Pt group metal compounds considered are the carbonyls of Rh, Os and Ru. (142 Refs.)

### Synthesis and Characterisation of Osmium Carbonyl Fluorides

S. A. BREWER, J. H. HOLLOWAY and E. G. HOPE, *J. Chem. Soc., Dalton Trans.*, 1994, (7), 1067–1071

The controlled oxidative fluorination of [Os<sub>3</sub>(CO)<sub>12</sub>] with XeF<sub>2</sub> in anhydrous HF solution yielded *cis*-[Os(CO)<sub>2</sub>F<sub>2</sub>] as the major product with [Os(CO)<sub>2</sub>F]<sup>+</sup>, [Os<sub>2</sub>(CO)<sub>7</sub>F<sub>4</sub>] and [Os<sub>2</sub>(CO)<sub>6</sub>F<sub>3</sub>]<sup>+</sup> as minor products which were characterised by <sup>13</sup>C, <sup>19</sup>F and <sup>13</sup>C-<sup>19</sup>F NMR spectroscopies. The Xe gas generated was vented off and removal of the HF solvent *in vacuo* yielded the tetrameric [Os(CO)<sub>2</sub>F<sub>2</sub>]<sub>4</sub>.

## ELECTROCHEMISTRY

### Microstructural Effects on Electrocatalytic Oxygen Reduction Activity of Nano-Grained Thin-Film Platinum in Acid Media

J. A. POIRIER and G. E. STONER, *J. Electrochem. Soc.*, 1994, **141**, (2), 425–430

The effect of microstructure and morphology on the O<sub>2</sub>-reduction activity of sputtered polycrystalline thin-film Pt deposits on C was studied using rotating-disk-electrode techniques in 1 M H<sub>2</sub>SO<sub>4</sub> at 25°C. The thin Pt films/C are a unique form of Pt for use in catalyst studies and to attain microstructures similar to those of dispersed Pt/C and for diffusion data studies. Thin-film Pt has a reduced lattice parameter at very small grain size. Mass activity and specific activity at 0.9 V vs. RHE both decrease with increasing grain size. The activity behaviour was attributed to the changes in electronic and geometric properties.

### Electrocatalytic Oxidation of Methanol and C1 Molecules on Highly Dispersed Electrodes. Part 1: Platinum in Polyaniline

H. LABORDE, J.-M. LÉGER and C. LAMY, *J. Appl. Electrochem.*, 1994, **24**, (3), 219–226

Electrodes of polyaniline film modified by dispersed Pt particles showed higher activity for the electrocatalytic oxidation of MeOH and other C1 molecules, such as formaldehyde and formic acid, than bulk Pt electrodes. Electrodes are conducting even at 0.0 V vs. RHE during oxidation of H at low potentials. The rate constant is increased greatly by the Pt dispersion. MeOH electro-oxidation was first order with respect to MeOH and the main oxidation product is formaldehyde.

### Electrochemical Reduction of Anthracenes on Poly(vinylferrocenium) Coated Pt Electrodes in Acetonitrile

H. GÜLCE, H. ÖZYÖRÜK and A. YILDIZ, *Ber. Bunsenges. Phys. Chem.*, 1994, **98**, (2), 228–233

Studies of the electroreduction behaviour of anthracene and some of its derivatives on poly(vinylferrocenium) coated Pt electrodes were made using cyclic voltammetry in acetonitrile/0.1 M TBAP solutions and compared to those on uncoated Pt. Catalytic reduction of the anthracene derivatives occurred on the coated surface showing that the catalytic processes are operating for the dianion and the anion radical of this compound.

### Methanol Oxidation on Carbon-Supported Pt-Sn Electrodes in Silicotungstic Acid

A. S. ARICÒ, H. KIM, A. K. SHUKLA, M. K. RAVIKUMAR, V. ANTONUCCI and N. GIORDANO, *Electrochim. Acta*, 1994, **39**, (5), 691–700

The electro-oxidation of MeOH was studied on Pt-Sn/C electrodes in silicotungstic acid (SiWA). XPS studies showed a lower amount of PtO species in the Pt-Sn/C catalyst with respect to the corresponding Pt/C sample. The steady-state galvanostatic polarisation data showed that a one-electron process is the rate determining step. The performance of the electrodes in 0.084 M SiWA was better than in 2.5 M H<sub>2</sub>SO<sub>4</sub> up to load currents of ~100 mA/cm<sup>2</sup> indicating the promoting behaviour of the electrolyte.

### Kinetics of Lateral Electron Hopping in Osmium-tris-4,7-diphenylphenanthroline Perchlorate Monolayers at the Air/Water Interface

D. H. CHARYCH, D. J. ANVAR and M. MAJDA, *Thin Solid Films*, 1994, **242**, (1–2), 1–6

Electron transfer kinetics are discussed involving electrochemical measurements of current due to diffusive, lateral electron hopping in Langmuir monolayers of Os(DPP), centres at the air/H<sub>2</sub>O interface. The Os(DPP), are locked in 2-D aggregates and have no lateral mobility. This novel approach allows the alteration of the solvation environment of the Os(DPP), molecules at the air/water interface by injecting small quantities of a particular solvent into the aqueous sub-phase. A strong dependence of the electron hopping rate constant on the morphology of the Os(DPP), monolayer films at the air/H<sub>2</sub>O interface is also reported.

## PHOTOCONVERSION

### Photochemical Elimination of Singlet Oxygen from Iridium Peroxo Complexes

M. SEIP and H.-D. BRAUER, *J. Photochem. Photobiol. A: Chem.*, 1994, **79**, (1-2), 19-24  
Vaska's compound,  $\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2(\text{O}_2)$  (1) was found to eliminate singlet O (3%) by irradiation, which is contrary to previously obtained data. The Ir (1) compound was photolysed by a 308 nm laser pulse in degassed solvents and the singlet O was detected by its emission at 1276 nm. Related complexes, with Br and I in place of Cl, also produced detectable amounts of singlet O.

### Photochemistry of the Luminescent Alkyl Complexes Alkyl(carbonyl)bis(triarylphosphine)(maleonitriledithiolato)iridium, $\text{IrR}(\text{CO})(\text{PAr}_3)_2(\text{mnt})$

P. BRADLEY, G. SUARDI, A. P. ZIPP and R. EISENBERG, *J. Am. Chem. Soc.*, 1994, **116**, (7), 2859-2868  
A number of luminescent alkyl complexes of formula  $\text{IrR}(\text{CO})\text{L}_2(\text{mnt})$ , where mnt = maleonitriledithiolate, R = Me, Et, Pr and  $\text{CH}_2\text{CN}$  and L is a triarylphosphine, were characterised. The complexes have octahedral co-ordination geometries with the phosphine ligands in mutually *trans* positions. Luminescence is observed at ~ 700 nm. The luminescence of the complexes in fluid solution is similar to the vibronic structure characteristic of other square-planar mnt complexes. Photolysis of  $\text{IrMe}(\text{CO})(\text{PPh}_3)_2(\text{mnt})$  in the presence of H-atom sources and radical traps gives products consistent with Ir-alkyl bond homolysis.

### Luminescence Behaviour of C120-Ru(bpy)<sub>2</sub><sup>2+</sup> Donor-Quencher Pair in Aqueous Solutions

J. T. KUNJAPPU, *J. Photochem. Photobiol. A: Chem.*, 1994, **78**, (3), 237-240  
The quenching of the fluorescence emission of 7-amino-4-methyl-coumarin (C120) by tris(2,2'-bipyridine)Ru(II) (1) was investigated in aqueous solutions to determine the mechanistic nature of the quenching. Stern-Volmer plots obtained from steady state and lifetime studies revealed a static quenching mechanism. The ground state association constant was  $2.0 \times 10^4/\text{mol}$ .

### Enantioselective and Photocatalytic Oxidation of 1,1'-Bi-2-Naphthol with a Chiral Ruthenium Complex which Includes Molecular Helicity

T. HAMADA, H. ISHIDA, S. USUI, K. TSUMURA and K. OHKUBO, *J. Mol. Catal.*, 1994, **88**, (1), L1-L5  
1,1'-Bi-2-naphthol was oxidised catalytically and enantioselectively with ≤ 15.2% e.e. by using the chiral Ru complex,  $\Delta\text{-}[\text{Ru}(\text{menbpy})_2]^{2+}$ , where menbpy = 4,4'-dimenthoxy carbonyl-2,2'-bipyridine, which has a strong redox ability as a photocatalyst and  $[\text{Co}(\text{acac})_3]$  as an oxidant under photoirradiation. The photo-oxidation of axial symmetrical (R)-(+)- and (S)-(-)-1,1'-bi-2-naphthols (a precursor of chiral BINAP) by this chiral Ru photocatalyst is the first report of such enantioselective oxidation of organic substrates.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Growth of Iridium Films by Metal Organic Chemical Vapour Deposition

T. GERFIN, W. J. HÄLG, F. ATAMNY and K.-H. DAHMEN, *Thin Solid Films*, 1994, **241**, (1-2), 352-355  
Thin films of metallic Ir were prepared by thermal MOCVD on quartz using the Ir complex,  $\text{Ir}(2,2,6,6\text{-tetramethyl-3,5-heptadione})(1,5\text{-cyclooctadiene})$ , as the Ir source. The complex could be evaporated at 115-140°C. MOCVD growth experiments were catalysed by an Ir-coated graphite susceptor and a reaction gas containing isopropanol, giving growth rates of 0.25 μm/h. The films were pure metallic and had a C and O content of ~ 1% and a typical sheet resistance of 50 μΩ/□. A three-dimensional growth mechanism was indicated.

## APPARATUS AND TECHNIQUE

### Multiple-Wavenumber Photoelectron Holography of Pt(111)

B. L. PETERSEN, L. J. TERMINELLO, J. J. BARTON and D. A. SHIRLEY, *Chem. Phys. Lett.*, 1994, **220**, (1,2), 46-52  
Using a Pt(111) surface based on the 4f<sub>7/2</sub> peak, 3-dimensional images, agreeing qualitatively with the known crystal structure, can be obtained directly from experimental photoelectron intensity patterns. Phase-summing over 8 intensity patterns over the range  $k = 8.8\text{-}10.2/\text{\AA}$  yielded a substantial reduction in conjugate image intensity, relative to images taken at single wavenumbers. This photoelectron holography, based on synchrotron radiation and forward scattering, is directly applicable to surface, near-surface interface systems, interface and deep-surface systems.

### Electrochemical Investigations of a Carbon Monoxide-Oxygen Sensor

Z. LUKACS, M. SINZ, G. STAIKOV, W. J. LORENZ, G. BAIER and A. VOGEL, *Solid State Ionics*, 1994, **68**, (1, 2), 93-98  
The  $\text{CO}$ ,  $\text{O}_2$ ,  $\text{PtAu/ZrO}_2(0.92)\text{Y}_2\text{O}_3(0.04)\text{Yb}_2\text{O}_3(0.04)/\text{Pt}$ , air system which functions as a  $\text{CO}$ ,  $\text{O}_2$  sensor, was studied. The polarisation resistance decreases with increasing  $P_{\text{CO}}/P_{\text{O}_2}$  ratio at constant  $P_{\text{O}_2}$ . Electrochemical impedance spectroscopy measurements were used to separate electrochemical reaction steps from the heterogeneous chemical steps, and  $\text{CO}$  oxidation was found to be an electrochemical step, agreeing with prior results for pure Pt paint electrodes.

### pH Measurements Based on a Palladium Electrode

M. SHAO, X. XING and C.-C. LIU, *Electroanalysis*, 1994, **6**, (3), 245-249  
A metal Pd electrode was tested as a pH sensor in near-neutral air-saturated aqueous solutions. Measurements were carried out with an 'on-site' pre-cleaning step and a potential decay process which used the pseudotransit potentials, instead of the steady-state potentials, to indicate the pH value of the solutions. The results had excellent reproducibility and a linear pH response with a sensitivity of ~ 60 mV/pH.

## A Hydrogen Sensor Based on the Optical Generation of Surface Plasmons in a Palladium Alloy

B. CHADWICK, J. TANN, M. BRUNGS and M. GAL, *Sens. Actuators B*, 1994, 17, (3), 215–220

A method for detecting H<sub>2</sub> concentrations near the explosive limit using the non-invasive optical generation of surface plasmons in a thin Pd-6% Ni film (50–400 Å) on a glass prism is described. H<sub>2</sub> is absorbed by the Pd-Ni which is used to reflect light from a light source, such as a LED or laser diode. The reflected intensity is measured as a function of the angle of the coated prism assembly which is kept in N<sub>2</sub>. Absorption of H<sub>2</sub> by the Pd alloy produced a 6.6 % change in the reflected light for a 1 % change in H<sub>2</sub> concentration. The sensor is highly reliable at 0.1–10 % H<sub>2</sub> concentrations.

## Characteristics of Monolayers of Ferrocene Derivatives and Estimation of Electrical Double Layers Formed in Langmuir Films

T. KONDO, R. C. AHUJA, D. MÖBIUS and M. FUJHIRA, *Bull. Chem. Soc. Jpn.*, 1994, 67, (2), 315–320

A Langmuir-Blodgett trough was used to form a multilayer comprised of more than two monolayers, so that the inner potential difference (pd) of the electrical double layer could be measured. Three kinds of ferrocene amphiphiles acted as the electron donor layer (D). The sensitiser monolayer (S) was a mixed [Ru(bpy)<sub>3</sub>]<sup>2+</sup> complex with a long alkyl fatty acid. The pd between the charged head group of the amphiphile and its counterion at the H<sub>2</sub>O-air interface was consistent with the electrical double-layer effect on the luminescent lifetime of the Ru complex in the (S) and (D) contacted monolayers.

## Electrocatalytic Flow Detection of Amino Acids at Ruthenium Dioxide-Modified Carbon Electrodes

J. WANG and Y. LIN, *Electroanalysis*, 1994, 6, (2), 125–129

The application of RuO<sub>2</sub>-modified C paste and graphite epoxy electrodes for the fixed-potential anodic detection of amino acids and peptides is reported. Optimal detection is obtained under strongly alkaline conditions and a low (+0.45 V vs. Ag/AgCl) operating potential. With flow injection, the response is fast, linear and reproducible.

## HETEROGENEOUS CATALYSIS

### The Function of Basicity on Pt/L Zeolite Reforming Catalyst

X. JIANG, Z. GAO, Z. RUAN, J. HUANG, Y. XU and X. GUO, *J. Fuel Chem. Technol. (China)*, 1994, 22, (1), 9–15

The effect of basicity of Pt/ML (M = Li, Na, K, Rb) zeolite catalysts on their performance was studied using the aromatisation of *n*-C<sub>6</sub> as a test reaction. Four different kinds of surface site with different basic strengths and metal-support electronic interactions were identified. The selectivity of the catalysts was LiL < NaL < KL < RbL in parallel with the increasing metal-support interaction in the Pt/ML catalysts.

## NO-CO Activity and Selectivity over a Pt<sub>10</sub>Rh<sub>90</sub>(111) Alloy Catalyst in the 10-Torr Pressure Range

K. Y. S. NG, D. N. BELTON, S. J. SCHMIEG and G. B. FISHER, *J. Catal.*, 1994, 146, (2), 394–406

Studies were performed of the effects of temperature, NO conversion and NO:CO ratio on the activity and selectivity of the NO-CO reaction over a Pt<sub>10</sub>Rh<sub>90</sub>(111) (1) surface. The NO-CO activity over (1) is similar to that over the Rh(111) surface at 573–648 K in that the reaction orders, products and selectivities are the same. The turnover numbers for (1) are slightly lower than for Rh(111), but the rates per surface Rh atom are nearly unchanged. It is concluded that the N<sub>2</sub>O selectivity and the overall reaction rate are controlled by the NO adsorption/desorption equilibrium.

## Solid Superacid as the Support of a Platinum Catalyst for Low-Temperature Catalytic Combustion

A. ISHIKAWA, S. KOMAI, A. SATSUMA, T. HATTORI and Y. MURAKAMI, *Appl. Catal. A: Gen.*, 1994, 110, (1), 61–66

An aqueous solution of Pt(NO<sub>2</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub> was impregnated into various single and mixed oxides and solid superacid supports which were then characterised and tested for the low temperature catalytic combustion of propane. The effects of pretreatments were examined. It was found that catalytic activity strongly depended on the support material acidity, the activity being higher on a support of stronger acidity. Solid superacids, SO<sub>4</sub><sup>2-</sup>-doped oxides of ZrO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>, were the best and provided high activity at temperatures around 523 K. The acidic support seems to prevent oxidation of supported Pt.

## Mixture Effects and Methanol Oxidation Kinetics over a Palladium Monolith Catalyst

T. F. BREWER, M. A. ABRAHAM and R. G. SILVER, *Ind. Eng. Chem. Res.*, 1994, 33, (3), 526–533

MeOH oxidation was studied using a simulated MeOH fuelled vehicle exhaust on a commercial Pd catalyst supported on a γ-Al<sub>2</sub>O<sub>3</sub> based washcoat and a cordierite monolith. The presence of H<sub>2</sub>O and CO greatly inhibited MeOH conversion, while propylene addition had no effect. At low temperature, and under reducing conditions, the MeOH conversion showed a local maximum, which was attributable to a shift in the oxidation state of the Pd catalyst within the temperature range of the MeOH oxidation reaction.

## An Efficient Heterogenised Palladium Catalytic System for the Reductive Carbonylation of Nitrobenzene to Methyl *N*-Phenylcarbamate

B. M. CHOUDARY, K. KOTESWARA RAO, S. D. PIROZHKOV and A. L. LAPIDUS, *J. Mol. Catal.*, 1994, 88, (1), 23–30

A montmorillonitebipyridine Pd(II) acetate complex catalyst has been found which is highly active and selective for the reductive carbonylation of nitrobenzene to methyl *N*-phenylcarbamate. The catalyst is reusable for several cycles, has consistent activity and selectivity and is easily filterable. It can become a practical alternative to other systems in current use.

## Nafion Supported Cationic Palladium Complexes as Catalysts

A. J. SEEN, K. J. CAVELL, A. W.-H. MAU and A. M. HODGES, *J. Membrane Sci.*, 1994, 87, (1 + 2), 149–157

Three cationic palladium co-ordination complexes, Pd(1,10-phen)<sub>2</sub><sup>2+</sup> (1), Pd(2,2'-bipy)<sub>2</sub><sup>2+</sup> (2) and Pd(1,10-phen)(py)<sub>2</sub><sup>2+</sup> (3), were immobilised in Nafion-H<sup>+</sup> and Nafion-Na<sup>+</sup> by ion-exchange. No changes occurred on immobilisation of (1) and (2) in Nafion. Ion-exchange of these Pd species into Nafion was nearly quantitative with > 95% of the cations extracted from solution. Partial decomposition of (3) occurred in Nafion-H<sup>+</sup> giving 1,10-phen and pyridine. The ability of immobilised species to dimerise ethene depended on the basicity of the N-donor ligand and the counterion in the Nafion.

## Methylcyclohexane Dehydrogenation on Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Catalysts

P. REYES, F. ORELLANA and G. PECCHI, *J. Chem. Technol. Biotechnol.*, 1994, 59, (3), 233–236

The effect of the Rh loading on the surface and catalytic properties of a series of 0.5–7.0 wt.% Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts was studied during methylcyclohexane dehydrogenation, and an unusual enhancement in catalytic activity in the well dispersed catalyst was found. The relationship between particle size, surface composition and turnover number in the dehydrogenation of methylcyclohexane is discussed. The results showed that the differences in catalytic behaviour during the dehydrogenation can be explained by electron-deficient Rh clusters, especially when the metal particle size becomes < 15 Å.

## Role of Support in Reforming of CH<sub>4</sub> with CO<sub>2</sub> over Rh Catalysts

J. NAKAMURA, K. AIKAWA, K. SATO and T. UCHIJIMA, *Catal. Lett.*, 1994, 25, (3,4), 265–270

Methane reforming with CO<sub>2</sub> over Rh supported on Al<sub>2</sub>O<sub>3</sub> (1), TiO<sub>2</sub> (2) and SiO<sub>2</sub> (3) at 550–1000 K was studied, and produced catalytic activity in the order (1) > (2) > (3). The activity of Rh/SiO<sub>2</sub> was increased by physically mixing with metal oxides, such as (1), (2) or MgO, indicating a synergistic effect. The role of the metal oxides used as the Rh support and the physical mixing may be ascribed to promoting the dissociation of CO<sub>2</sub> on the Rh surface, since the CH<sub>4</sub> + CO<sub>2</sub> reaction is first order in CO<sub>2</sub> pressure, suggesting that CO<sub>2</sub> dissociation is the rate determining step.

## Catalytic Hydrogenation of Carbon Monoxide over Silica-Supported Ir-Mo-Rh Catalyst

T. MATSUMOTO, W. Y. KIM, M. KISHIDA, H. NAGATA and K. WAKABAYASHI, *Catal. Lett.*, 1994, 24, (3,4), 391–394

Studies of the effect of Rh additions to Ir-Mo/SiO<sub>2</sub> catalysts, showed a remarkable increase in activity with small additions of Rh, for CO hydrogenation (1), even though CO conversion over 1 wt.% Rh/SiO<sub>2</sub> monometallic catalyst was very low. The catalysts had higher activity for (1) than Ir-Mo bimetallics. The activity was affected by the metal impregnation procedure in the catalyst during preparation. Selectivity to alcohols did not change much upon Rh addition.

## Hydrogen Chemisorption on Potassium Promoted Supported Ruthenium Catalysts

D. O. UNER, M. PRUSKI, B. C. GERSTEIN and T. S. KING, *J. Catal.*, 1994, 146, (2), 530–536

The effect of K promotion on H chemisorption for a number of Ru/SiO<sub>2</sub> catalysts prepared by sequential and co-impregnation methods was studied by proton NMR spectroscopy. K was incorporated on the support by exchange with the Si(OH) groups forming Si(OK) species. However, the sequential impregnation technique was more efficient. K addition decreased the amount of both H adsorbed on the metal and the support hydroxyl groups.

## Effect of the Method of Preparing Ru-Mo/SiO<sub>2</sub> Catalysts in Their Behaviour in CO Hydrogenation

M. J. PEREZ ZURITA, I. S. HENRIQUEZ, M. R. GOLDWASSER, M. L. CUBEIRO and G. C. BOND, *J. Mol. Catal.*, 1994, 88, (2), 213–222

Ru catalysts were prepared by sequential impregnation of SiO<sub>2</sub> by RuCl<sub>3</sub> and then by (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>, followed by drying and reduction in H<sub>2</sub> at 623 K. The best selectivity to oxygenates was displayed by catalysts where the surface of the Ru particles is partially covered by Mo-oxo species, with the greatest effect being achieved when RuCl<sub>3</sub> was introduced first. The number of large groups of free Ru atoms needs to be minimised if hydrocarbon formation is to be suppressed, but this process may occur on top of oxo-Mo species activated by underlying Ru atoms.

## Ruthenium Supported on Zeolite A: Preparation and Characterisation of a Stable Catalyst for Ammonia Synthesis

J. WELLENBÜSCHER, M. MUHLER, W. MAHDI, U. SAUERLANDT, J. SCHÜTZE, G. ERTL and R. SCHLÖGL, *Catal. Lett.*, 1994, 25, (1,2), 61–74

Impregnation of Na-A or K-A zeolite with Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> in aqueous solution resulted in a purple precursor catalyst containing oligomeric Ru-oxo complexes with a mixture of amino and hydroxo/oxo ligands. Controlled thermal activation under H<sub>2</sub> converted the precursor in a two-stage process into an active catalyst with good long-term stability and resistance against small doses of O poison. Several nanometre-sized Ru metal particles bonded to the zeolite, in the K form, provided an alkali promoter at the interface.

## Alcohol Synthesis by CO<sub>2</sub> Hydrogenation over Heterogeneous Ru-Cu Catalyst. 1. Influence of Bimetal Exchange Order and Ion-Exchange Solution pH Value

Y. JI, X. YIN and C. WANG, *J. Fuel Chem. Technol. (China)*, 1994, 22, (1), 53–57

Studies of the effect of the exchange order of bimetal on activity were performed on Ru-Cu heterogeneous catalyst prepared by an ion-exchange method, under 3.0 MPa, CO<sub>2</sub> : H<sub>2</sub> = 1 : 1.5, at 413 K. Higher catalyst activity was obtained on catalysts using a bimetal exchange order of first Cu followed by Ru. Increased catalyst activity occurred under alkaline conditions. The lower valence metal element was the active catalyst constituent.

### The Oxidation of Alcohols and Aldehydes by Potassium Chlorate in the Presence of a Ruthenium Heteropoly-Complex

L. I. KUZNETSOVA, V. A. LIKHOLOBOV and L. G. DETUSHEVA, *Kinet. Katal.*, 1993, 34, (6), 1017–1019  
Studies of the catalytic properties of the heterocomplex  $\text{Ru(IV)} + \text{KClO}_4$ , were performed during the oxidation of primary alcohols and aldehydes in aqueous solutions. The catalyst which was prepared by the interaction of  $\text{K}_2\text{RuOHCl}$  with  $\text{Na}_7\text{PW}_{11}\text{O}_{39}$ , was active and selective during K chlorate oxidation of primary alcohols giving the corresponding carboxylic acid in 100% yield in an aqueous solution with pH 2 at 25–75°C. The oxidation of acrolein in the presence of the catalyst produced acrylic acid with high selectivity.

## HOMOGENEOUS CATALYSIS

### In Situ IR Studies of a Phosphine-Palladium Catalyst for the Hydrocarboxylation of Olefins

YU. G. NOSKOV, M. I. TEREKHOVA and E. S. PETROV, *Kinet. Katal.*, 1993, 34, (6), 1001–1004  
In situ IR studies of the hydrocarbonylation of ethylene and alcohol to dioxane in the presence of  $\text{PdCl}_2(\text{Ph}_3\text{P})_2$  were performed under CO pressures of 0.8–2.4 MPa at 100–110°C. Absorption bands of 1680, 1980 and 2020/cm were found for Pd complexes  $(\text{RCO})\text{PdCl}(\text{Ph}_3\text{P})_2$  (where  $\text{R}=\text{C}_2\text{H}_5$ ,  $\text{PhC}_2\text{H}_4$ ),  $\text{Pd}(\text{CO})(\text{Ph}_3\text{P})_2$  and  $\text{Pd}(\text{CO})_2(\text{Ph}_3\text{P})_2$ , respectively. Changes in IR-spectra occurring during changes in the reagent contents and pressures were observed.

### A Flexible and Rational Synthesis of Substituted Triphenylenes by Palladium-Catalysed Cross-Coupling of Arylzinc Halides

R. C. BORNER and R. F. W. JACKSON, *J. Chem. Soc., Chem. Commun.*, 1994, (7), 845–846  
A new, flexible route to substituted unsymmetrical triphenylenes, has been developed which involves the preparation of terphenyls using a Pd-catalysed cross-coupling of arylzinc halides with 1,2-dihalogenobenzenes, followed by oxidative cyclisation of the terphenyls using ferric chloride.  $\text{Pd}_2(\text{dba})_3$  catalyst is used together with  $\text{PPh}_3$ , THF, reflux;  $\text{FeCl}_3$ , concentrated  $\text{H}_2\text{SO}_4$  (trace),  $\text{CH}_2\text{Cl}_2$ , at room temperature followed by MeOH quench. This method is effective for the synthesis of triphenylene derivatives in which each of the original aromatic starting materials is different.

### Palladium Complex-Potassium Carbonate-Catalysed Reductive Carbonylation of Mono- and Di-nitroaromatic Compounds

N. P. REDDY, A. M. MASDEU, B. EL ALI and H. ALPER, *J. Chem. Soc., Chem. Commun.*, 1994, (7), 863–864  
A catalytic amount of  $\text{K}_2\text{CO}_3$  can promote the Pd-catalysed reductive carbonylation of mono- and di-nitro aromatic compounds in MeOH under mild conditions, to give mono- and di-urethanes in good yields. The reaction of mono- and di-nitroaromatic compounds with CO in benzene and MeOH, in the presence of 1,3-bis(diphenylphosphino)propane Pd dichloride and  $\text{K}_2\text{CO}_3$ , yielded diurethanes.

### Hydroformylation of Olefins Catalyzed by (1,5-Cyclooctadiene) Salicylaldoximato-rhodium under Atmospheric Pressure

W. CHEN, Y. XU and S. LIAO, *J. Mol. Catal.*, 1994, 88, (3), 277–286  
Hydroformylation of vinylarenes, alkenes and cyclic olefins was carried out using the title compound  $\text{Rh}(\text{SOX})(\text{COD})$  as catalyst precursor at 0.1 MPa and 60°C in toluene. Adding phosphine or phosphite ligands determines reaction rate and regioselectivity, and combining  $\text{Rh}(\text{SOX})(\text{COD})$  with diphosphine ligands was more active in vinylarene hydroformylation, whereas with monophosphine ligands alkene hydroformylation was favoured. Using diphosphine increased the formation of branched aldehydes in both the hydroformylation of vinylarenes and alkenes.

### Direct Catalytic Conversion of Methane to Acetic Acid in an Aqueous Medium

M. LIN and A. SEN, *Nature*, 1994, 368, (6472), 613–615  
A direct high-yield production of acetic acid from  $\text{CH}_4$  is reported, using a mixture of  $\text{CH}_4$ , CO and  $\text{O}_2$  in the presence of  $\text{RhCl}$ , dissolved in  $\text{H}_2\text{O}$  at 100°C. The acetic acid yield was increased by adding  $\text{I}^-$  ions or 5% Pd/C. There was no significant decrease in catalytic activity after 400 h of reaction time.

### The Kinetics and Mechanism of Concurrent Reactions of Acetylene Hydrogenation and Hydroiodination by Rh(III)-H<sup>-</sup>-I<sup>-</sup>-H<sub>2</sub>O

S. A. MITSHENKO, V. V. ZAMASHCHIKOV, E. L. KOSTENKO and K. V. MALAKHOV, *Kinet. Katal.*, 1993, 34, (6), 1012–1016  
Studies of the kinetics and mechanism of new catalytic reactions of hydroiodination and reduction of acetylene to ethylene were performed in the presence of  $\text{Rh(III)-H}^--\text{I}^- - \text{H}_2\text{O}$  where I<sup>-</sup> is NaI. It is shown that the limiting stage of the studied acetylene conversion is the formation of a  $\sigma$ -vinyl Rh(III) complex as the result of a subsequent reaction of reversible formation of Rh(III) acetylide, reduction of  $\text{Rh(III)-C}\equiv\text{CH}$  iodide-ions to Rh(I) acetylide which gives, by protolysis, the  $\pi$ -acetylene Rh(I) complex. The dissolution of the latter complex is regenerated by acetylene, and protonation, both leading to the  $\sigma$ -vinyl Rh(III) complex. Vinyl iodide was produced during the decomposition of  $\text{Rh(II)-CH}=\text{CH}_2$  in the presence of I<sup>-</sup>.

### Homogeneous and Alumina Supported Rhodium Complex Catalyzed Hydrogenation

A. M. TRZECIAK, J. J. ZIÓLKOWSKI, Z. JAWORSKA-GALAS, W. MIŚTA and J. WRZYSZCZ, *J. Mol. Catal.*, 1994, 88, (1), 13–22  
The complex  $\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2$  was studied in homogeneous and heterogenised systems being supported on  $\gamma\text{-Al}_2\text{O}_3$ , and was used as catalyst precursor for hex-1-ene and benzene hydrogenation at 80°C and 6.5 atm of  $\text{H}_2$ . The hydride complexes,  $\text{HRh}(\text{CO})(\text{PPh}_3)_2$  and  $\text{HRh}(\text{CO})(\text{PPh}_3)$  were found to be the active forms in the homogeneous system. When  $\gamma\text{-Al}_2\text{O}_3$  supported  $\text{Rh}(\text{OH})(\text{CO})(\text{PPh}_3)_2$  complex was activated for 2 h in  $\text{H}_2$ , its catalytic activity was sustained for 4 weeks.

## Asymmetric Hydroformylation of 1,2-Disubstituted Olefins Catalysed by Chiral Phosphinephosphite-Rhodium(I) Complexes

N. SAKAI, K. NOZAKI and H. TAKAYA, *J. Chem. Soc., Chem. Commun.*, 1994, (4), 395–396

The highly enantioselective hydroformylation of 1,2-disubstituted olefins, such as (*E*)- and (*Z*)-but-2-ene, (*E*)- and (*Z*)-1-phenylprop-1-ene, indene and 1,2-dihydronaphthalene has been catalysed by the (*R,S*)-binaphos-Rh(I) complex: {(*R,S*)-binaphos = (*R*)-[2-(diphenylphosphino)-1,1'-binaphthalen-2'-yl] [(*S*)-1,1'-binaphthalen-2,2'-diyl]phosphite} or its enantiomer. The reaction gave the corresponding oxoaldehydes in  $\leq 97\%$  enantiomeric excess. This catalysis provides a new and powerful way to synthesise a number of physiologically active compounds.

## The Kinetics of the Reaction of [Ru(Cl)H(PPh<sub>3</sub>)<sub>3</sub>] with Various Olefins

G. ALIBRANDI and B. E. MANN, *J. Chem. Soc., Dalton Trans.*, 1994, (7), 951–954

The reaction of [Ru(Cl)H(PPh<sub>3</sub>)<sub>3</sub>] catalyst (1) with cycloheptatriene, cyclohepta-1,3-diene, cyclooctatetraene, penta-1,4-diene, cycloocta-1,5-diene and dimethyl maleate in CH<sub>2</sub>Cl<sub>2</sub> at 10°C proceeded by two mechanisms: dissociation of a PPh<sub>3</sub> ligand and by direct attack of the olefin on (1). The dissociation was the dominant mechanism.

## Preparation of Novel Poly(enol ester)s by Ruthenium Complex Catalyzed Polyaddition of Dicarboxylic Acids with Diynes

I. YAMAGUCHI, K. OSAKADA and T. YAMAMOTO, *Macromolecules*, 1994, 27, (5), 1112–1116

Terephthalic acid reacted with 1,7-octadiyne in the presence of a catalytic amount of Ru(cod)<sub>2</sub> (cod = 1,5- $\eta^2$ -cyclooctadienyl), PBU<sub>3</sub>, and maleic anhydride in DMF to give a poly(enol ester), [OCO-C<sub>6</sub>H<sub>4</sub>-COO-C(=CH<sub>2</sub>)-C<sub>6</sub>H<sub>4</sub>-C(=CH<sub>2</sub>)]<sub>n</sub> as a brown solid in 28% yield, by Markovnikov addition of the OH group to the C≡C triple bond. Polyaddition of acetylenedicarboxylic acid with 1,4-diethynylbenzene using the Ru(cod)<sub>2</sub> catalyst yielded poly(enol ester), [OCO-C≡C-COO-C(=CH<sub>2</sub>)-C<sub>6</sub>H<sub>4</sub>-C(=CH<sub>2</sub>)]<sub>n</sub>.

## FUEL CELLS

### Influence of the Supporting Electrolyte on the Oxygen Reduction Reaction at the Platinum/Proton Exchange Membrane Interface

J. B. FLORIANO, E. A. TICIANELLI and E. R. GONZALEZ, *J. Electroanal. Chem.*, 1994, 367, (1–2), 157–164

The O reduction reaction and the transport of the reactant through the membrane were studied at a Pt/proton exchange membrane (PEM) interface immersed in H<sub>2</sub>SO<sub>4</sub> + H<sub>3</sub>PO<sub>4</sub> mixtures, as functions of the electrolyte concentration and PEM film thickness. The results showed that at shorter and longer times, respectively, the Pt/PEM/liquid electrolyte interface tends to that of a pure Pt/PEM electrolyte system, and a Pt/liquid electrolyte system.

## High Performance Catalyzed-Reaction Layer for Medium Temperature Operating Solid Oxide Fuel Cells

M. WATANABE, H. UCHIDA, M. SHIBATA, N. MOCHIZUKI and K. AMIKURA, *J. Electrochem. Soc.*, 1994, 141, (2), 342–346

Catalyzed-reaction layers containing a very small amount of highly dispersed microcrystalline Pt group metal catalyst were tested for SOFC electrodes at various temperatures. With an electrolyte of solid Y<sub>2</sub>O<sub>3</sub>-stabilised ZrO<sub>2</sub>, a large anodic depolarising effect in H at 800°C was seen. The highest electrocatalytic activity at 800°C was obtained for Ru-dispersed samaria-doped CeO<sub>2</sub> (SDC) as anode based on catalyst weight, and for Pt-dispersed SDC based on catalyst surface area.

## Thick Film Ruthenium Oxide/Yttria-Stabilized Zirconia-Based Cathode Material for Solid Oxide Fuel Cells

M. HROVAT, J. HOLC and D. KOLAR, *Solid State Ionics*, 1994, 68, (1,2), 99–103

RuO<sub>2</sub>/YSZ (8% Y<sub>2</sub>O<sub>3</sub>, stabilised ZrO<sub>2</sub>)-based material was studied for SOFC cathodes by investigating sub-solidus phase equilibria in the binary RuO<sub>2</sub>-ZrO<sub>2</sub> system and ternary RuO<sub>2</sub>-ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> system. The electrical and microstructural characteristics at operating temperatures of SOFCs were stable. Thick film electrodes printed and fired on YSZ electrolyte had good adhesion, low sheet resistivity and a positive TCR.

## CORROSION PROTECTION

### Corrosion Behaviour of Platinum-Catalyzed Carbon in Phosphoric Acid Solution

S.-I. PYUN, Y.-G. RYU and S.-H. CHOI, *Carbon*, 1994, 32, (1), 161–164

The effects of gaseous O<sub>2</sub> on the corrosion behaviour of Pt-free and Pt-catalysed C electrodes were studied in 85% H<sub>3</sub>PO<sub>4</sub> (1) solution at 145°C and 0.7 V<sub>RHE</sub>. The faradaic reactions on the catalysed Pt were inhibited by the selective adsorption of iodide ions onto the Pt surface. The anodic current peak increased with increasing ageing time in the hot (1). O-blowing reduced the amount of the surface oxide.

## CHEMICAL TECHNOLOGY

### Thin Palladium Membrane Formed in Support Pores by Metal-Organic Chemical Vapor Deposition Method and Application to Hydrogen Separation

S. YAN, H. MAEDA, K. KUSAKABE and S. MOROOKA, *Ind. Eng. Chem. Res.*, 1994, 33, (3), 616–622

A thin Pd membrane can be formed inside the porous wall of an  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support tube by a MOCVD process in which the reaction temperature is continuously increased, by decomposition of Pd(II) acetate in Ar under reduced pressure. For a membrane prepared at  $\leq 300^\circ\text{C}$ , the H permeance and the selectivity to N at 300–500°C are higher than 0.1 mol/(m<sup>2</sup>s) and 1000, respectively. Repeated cycling at 100–300°C showed that the membrane is resistant to H embrittlement.

## Deactivation and Regeneration of Pd-Ag Membranes for Dehydrogenation Reactions

J. K. ALI, E. J. NEWSON and D. W. T. RIPPIN, *J. Membrane Sci.*, 1994, **89**, (1 + 2), 171-184

Studies performed on commercial Pd-Ag tubular membranes showed that the  $H_2$  permeability data were represented by Sievert's and Fick's laws. Initial exposure of the fresh membrane to methylcyclohexane (MCH), or toluene inhibited  $H_2$  permeation but this was restored after air oxidation. S and Cl poisoned the membrane but redox procedures for S and  $H_2O$  vapour treatment for Cl restored the original  $H_2$  permeation rates. A catalytic membrane reactor with a sulphided, monometallic, commercial catalyst for MCH dehydrogenation gives twice the equilibrium value of toluene.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Ultra-Low Resistance Base Ohmic Contact with Pt/Ti/Pt/Au for High- $f_{max}$ AlGaAs/GaAs Heterojunction Bipolar Transistors

T. SUGIYAMA, Y. KURIYAMA, M. ASAKA, N. IIZUKA, T. KOBAYASHI and M. OBARA, *Jpn. J. Appl. Phys.*, 1994, **33**, Part 1, (1B), 786-789

A very low contact resistivity of  $4.2 \times 10^{-7} \Omega \text{ cm}^2$  was obtained for ohmic contacts of a 500 Å thick  $p\text{-Al}_{0.1}\text{Ga}_{0.9}\text{As}$  layer formed to a Pt/Ti/Pt/Au system, which was thermally stable at 350°C. The optimum Pt thickness was ~ 50 Å and a high  $f_{max}$  of 160 GHz was achieved for AlGaAs/GaAs heterojunction bipolar transistors (HBTs) using Pt/Ti/Pt/Au base electrodes. A multiplexer IC operated well with these high- $f_{max}$  HBTs up to 40 Gbps, which is the highest speed reported; limited only by the measuring device.

### Thermal Stability of Ti/Pt/Au Nonalloyed Ohmic Contacts on InN

F. REN, C. R. ABERNATHY, S. J. PEARTON and P. W. WISK, *Appl. Phys. Lett.*, 1994, **64**, (12), 1508-1510

Non-alloyed Ti/Pt/Au ohmic contacts on  $n$ -type InN were stable at  $\leq 300^\circ\text{C}$ , with extremely low contact resistivity. The contacts were annealed at  $\leq 420^\circ\text{C}$  to study their thermal stability. A contact resistivity of  $1.8 \times 10^{-7} \Omega \text{ cm}^2$  which was measured at room temperature was found to be due to the extremely high doping level in the InN. After  $300^\circ\text{C}$  annealing, the contact resistivity increased to  $2.4 \times 10^{-7} \Omega \text{ cm}^2$ . After annealing at  $420^\circ\text{C}$  serious degradation of the contacts occurred, due to decomposition of the InN film.

### Magnetic Properties of $\text{Co}_x\text{Ni}_{1-x}/\text{Pt}$ Multilayers

R. KRISHNAN, H. LASSRI, M. SEDDAT, M. PORTE and M. TESSIER, *Appl. Phys. Lett.*, 1994, **64**, (17), 2312-2314

Magnetic and magneto-optical properties of  $\text{Co}_x\text{Ni}_{1-x}/\text{Pt}$  multilayers prepared by evaporation under ultrahigh vacuum conditions have been studied. The addition of Co to Ni produce an increase in both the surface anisotropy and  $T_c$ . In  $\text{Co}_{0.3}\text{Ni}_{0.7}/\text{Pt}$  multilayers, for  $t(\text{Co,Ni}) = 0.45 \text{ nm}$ , a perpendicular  $M\text{-}H$  loop with a good rectangularity and coercivity of 1 kOe and  $T_c$  of  $180^\circ\text{C}$  were observed.

## Au/Pd/Te Ohmic Contacts on $n$ -Type InP

P. A. LEIGH, R. M. COX and P. J. DOBSON, *Solid-State Electron.*, 1994, **37**, (7), 1353-1358

Studies of Au/Pd/Te contacts on  $n$ -type InP showed that a contact resistance of  $1 \times 10^{-4} \Omega \text{ cm}^2$  was achieved on a doping level of  $4 \times 10^{19}/\text{cm}^3$  and  $1 \times 10^{-6} \Omega \text{ cm}^2$  on  $4 \times 10^{18}/\text{cm}^3$ . The contact quickly became ohmic upon annealing with lower resistance as the anneal temperature was increased. Pd acted as a barrier during annealing preventing interaction of the Te and Au, and giving a post processing resistivity of  $18 \mu\Omega \text{ cm}$  for the ohmic contact metallisation.

## High-Temperature Stable Ir-Al/ $n$ -GaAs Schottky Diodes

T. LALINSKÝ, D. GREGUŠOVÁ, Ž. MOZOLOVÁ, J. BREZA and P. VOGRINCIC, *Appl. Phys. Lett.*, 1994, **64**, (14), 1818-1820

Ir-Al/GaAs Schottky contacts, based on a sequentially evaporated Ir-Al bimetallic system and containing ~ 25 at.% Al have excellent thermal stability, and are stable at  $\leq 950^\circ\text{C}$  for 10 s. The barrier height is enhanced with the temperature of annealing, and an interfacial graded layer of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  is formed by exchange of Al and Ga by interdiffusion between the Ir-Al film and GaAs substrate. The material is useful as a gate material in GaAs HFETs and SAGFETs.

## TEMPERATURE MEASUREMENT

### Thin Film Platinum Resistance Thermometers: Calibration and Mathematical Description of $T(R)$ Function

D. A. DIMITROV, A. L. ZAHARIEV, J. K. GEORGIEV, G. A. KOLEV, J. N. PETRINSKI and T. IVANOV, *Cryogenics*, 1994, **34**, (6), 487-489

The temperature/resistance function and a mathematical description of three types of thin film Pt resistance thermometers were determined for the temperature range 77-300 K. The sensors could be used as low temperature thermometers with an accuracy of  $\pm 10 \text{ mK}$  after individual calibration. For measurement precision of  $< \pm 100 \text{ mK}$ , the sensors can be used without individual calibration, if  $R_0$  is known.

## MEDICAL USES

### Preclinical Toxicology and Tissue Platinum Distribution of Novel Oral Antitumour Platinum Complexes: Ammine/Amine Platinum(IV) Dicarboxylates

M. J. MCKEAGE, S. E. MORGAN, F. E. BOXALL, B. A. MURRER, G. C. HARK and K. R. HARRAP, *Cancer Chemother. Pharmacol.*, 1994, **33**, (6), 497-503

Six orally given anti-tumour Pt complexes with different alicyclic amine, axial dicarboxylate or leaving substituent groups were studied. Pt tissue levels in kidney, liver and other organs after dosage were compared with equal amounts of intravenously (iv) delivered cisplatin and carboplatin. Oral JM216 caused dose-limiting leucopenia but less gastrointestinal toxicity than (iv) cisplatin or carboplatin for the mouse.