

# ABSTRACTS

*of current literature on the platinum metals and their alloys*

## PROPERTIES

### An Experimental Test of Various Models of the Active Site for Nitric Oxide Reduction on Platinum

R. I. MASEL, *Catal. Rev.-Sci. Eng.*, 1986, **28**, (2&3), 335-369

Predictions of the reduction of NO have been examined using several models of the active site, namely the thermodynamic, geometric, atomic site and electronic structure models. Each model predicts which face of a Pt surface will be most active for the reduction. Among faces considered were (100), (111), (110), (410), (611) and (210). There is very little agreement between the various models. Experimental work on NO reduction was examined, and compared with the models. Experimentally Pt(410) is the most active face, and only the orbital symmetry model of electronic structure was reasonably in agreement with the data. (75 Refs.)

### Surface Topography of (100)-Type Electro-Faceted Platinum from Scanning Tunnelling Microscopy and Electrochemistry

J. GÓMEZ, L. VÁZQUEZ, A. M. BARÓ, N. GARCIA, C. L. PERDRIEL, W. E. TRIACA and A. J. ARVIA, *Nature*, 1986, **323**, (6089), 612-614

The first observation on (100)-type Pt electrodes in real-time by scanning tunnelling microscopy is reported. The existence of a faceted surface consisting of a flat part surrounded by ridge-type structures was confirmed. Initially cluster formation occurs which develops in a preferential orientation, thus giving direct evidence that faceting occurs through a selective electro-dissolution/electro-deposition process which may involve a fast diffusion of metallic species in the electrolyte or on the surface.

### Resistivity of the Heavy-Fermion U(Pt,Pd)<sub>3</sub> Alloys

R. VERHOEF, A. DE VISSER, A. MENOVSKY, A. J. RIEMERSMA and J. J. M. FRANSE, *Physica B + C*, 1986, **142**, (1), 11-15

Electrical resistivity measurements were taken on a series of mono- and polycrystalline U(Pt<sub>1-x</sub>Pd<sub>x</sub>)<sub>3</sub> compounds ( $x \leq 0.15$ ) in the temperature range 1.4-300K. On alloying with Pd the spin-fluctuation-like resistivity of pure UPt<sub>3</sub> transforms into a more complex curve for  $x=0.02$  and  $x=0.05$ , revealing transitions at 3.3K and 5.6K, respectively. At higher Pd concentrations ( $x=0.10, 0.15$ ), the resistivity curves change to a Kondo-type of behaviour. A second phase appears in the X-ray pattern in the same concentration range.

### Effect of Oxygen on the Electronic Properties of Pd

H. CLAUS and N. C. KOON, *Solid State Commun.*, 1986, **60**, (6), 481-484

Low field magnetisation measurements were taken of Pd-Fe alloys obtained by implanting Fe<sup>+</sup> into pure Pd foils and Pd foils pre-doped with B<sup>+</sup> and O<sup>+</sup>. Oxygen in solid solution in Pd reduces the Pd susceptibility at a rate of 25% per at.% O, exactly twice the rate of B.

### The Hydrogenation of CN on Pd(111) and Pd(100)

M. E. KORDESCH, W. STENZEL and H. CONRAD, *Surf. Sci.*, 1986, **175**, (1), L687-L692

Adsorbed CN may be produced on Pd(111) and Pd(100) surfaces at room temperature by dissociative adsorption of cyanogen. HREELS shows that adsorbed CN forms adsorbed HCN or DCN on these Pd surfaces by reaction with H adsorbed from the residual gas or by dosing with H<sub>2</sub> or D<sub>2</sub>. The reaction temperature is slightly lower for Pd(100) and the range of temperatures over which the reaction occurs is much smaller.

### Surface Enrichment of Rhodium in Pd-Rh Alloys after High Temperature Air Oxidation

B. M. JOSHI, H. S. GANDHI and M. SHELEF, *Surf. Coatings Technol.*, 1986, **29**, (3), 131-140

Foils of Pd-Rh alloys containing 85 and 95% Pd were heated in air between 600-1100°C and their surface compositions were examined. Surface enrichment of Pd as an oxide was observed for foils heated <800°C, whereas Rh enrichment occurred for foils heated between 850 and 950°C. For foils heated at 1000-1100°C a slight enrichment of Rh was observed. These surface changes can be attributed to thermodynamic differences in the formation and deposition of Pd and Rh oxides and to diffusion in thick surface oxides on Pd-rich alloys.

### Kinetics of Phase Transformation from Pd<sub>3</sub>Si to Pd<sub>2</sub>Si

T. CHIKYOW, I. OHDOMARI and S. SUZUKI, *Phys. Rev. B*, 1986, **34**, (7), 4807-4811

The phase transformation from Pd<sub>3</sub>Si to Pd<sub>2</sub>Si has been investigated. Pd<sub>3</sub>Si, initially formed by annealing an epitaxial Pd<sub>3</sub>Si layer on Si at 850°C, transformed to Pd<sub>2</sub>Si by a post annealing below 750°C. After the phase transformation, small grains of Pd<sub>2</sub>Si and Si were observed. 90% of the surface of the sample post annealed at 650°C was covered with Pd<sub>2</sub>Si grains, while only 75% of the surface area was covered with Pd<sub>2</sub>Si grains for the sample post annealed at 750°C.

### Interdiffusion and Compound Formation in the Mo/Pd/Si Thin Film Metallization System

R. N. SINGH, *Thin Solid Films*, 1986, **143**, (3), 249-257

Interdiffusion and compound formation in Mo/Pd/Si thin films were studied between 250-750°C by sheet resistance measurement, X-ray diffraction, AES and Rutherford backscattering spectrometry. Results indicated that thermal annealing in the Mo/Pd/Si thin film couples between 250-475°C leads to Pd-Si interactions, Pd<sub>2</sub>Si formation and thus a small increase in sheet resistance. For temperatures >475°C a Mo-Pd<sub>2</sub>Si interaction, besides the Pd-Si interaction, occurs; MoSi<sub>2</sub> was formed and a dramatic increase in sheet resistance occurred.

### Boiling Points and Ideal Solutions of Ruthenium and Osmium Tetraoxides

Y. KODA, *J. Chem. Soc., Chem. Commun.*, 1986, (17), 1347-1348

The boiling point of RuO<sub>4</sub> has been directly measured for the first time as 129.6±0.2°C which is identical to that of OsO<sub>4</sub>, namely 129.7±0.2°C. All mixtures of RuO<sub>4</sub> and OsO<sub>4</sub> had practically the same boiling point as the two components. RuO<sub>4</sub> and OsO<sub>4</sub> dissolve each other to make ideal solutions, which suggests that their physical and chemical properties are based mainly upon tetrahedrally coordinated O atoms in the outer shell rather than the central metal ion in the molecule.

### Superconductivity and Magnetism of bcc Cr-Ru Alloys

Y. NISHIHARA, Y. YAMAGUCHI, M. TOKUMOTO, K. TAKEDA and K. FUKAMICHI, *Phys. Rev. B*, 1986, **34**, (5), 3446-3449

Cr-Ru alloys containing 14-25at.%Ru, of b.c.c. structure, exhibited superconductivity below ~2K for concentrations of Ru >~17at.%. The magnetic susceptibility of these alloys peaked at ~170K and it is suggested that superconductivity co-exists with itinerant-electron antiferromagnetism in b.c.c. Cr-Ru alloys.

## CHEMICAL COMPOUNDS

### Palladium and Platinum

P. A. CHALONER, *Coord. Chem. Rev.*, 1986, **72**, 1-195  
A review of literature on Pt and Pd co-ordination chemistry published in 1983 and some from 1982 in *Chem. Abs.* is presented. Complexes considered include those of Pt(VI), Pd(VI), Pd(IV) and Pt(IV) with ligands from Groups IV, V, VI and VII, Pt(III) and Pd(III), Pt(II) and Pd(II) with similar ligands and Pd(I), Pt(I), Pd(0) and Pt(0) and those with mixed oxidation states. Literature on clusters of various types is examined, as is catalysis by Pt and Pd complexes where the amount of literature has increased. Sn-Pt complexes are considered. (787 Refs.)

### First Synthesis of a Nitro Complex of Ruthenium (III), as a Key Intermediate in the Oxidation of Nitro Ligand to Give both Nitrosyl and Nitrato Ligands

H. NAGAO, M. MUKAIDA, K. SHIMIZU, F. S. HOWELL and H. KAKIHANA, *Inorg. Chem.*, 1986, **25**, (23), 4312-4314

The first synthesis is reported of [RuX(NO<sub>2</sub>)(bpy)<sub>2</sub>]Y where (X=Cl, Y=ClO<sub>4</sub>), (X=Cl, Y=PF<sub>6</sub>), (X=Br, Y=ClO<sub>4</sub>) or (X=Br, Y=PF<sub>6</sub>), by the oxidation of the corresponding nitrosyl complex with NaClO solution.

## ELECTROCHEMISTRY

### Stabilization of RuO<sub>2</sub> by IrO<sub>2</sub> for Anodic Oxygen Evolution in Acid Media

R. KÖTZ and S. STUCKI, *Electrochim. Acta*, 1986, **31**, (10), 1311-1316

Anodic O<sub>2</sub> evolution on Ru<sub>x</sub>Ir<sub>1-x</sub>O<sub>2</sub> was investigated for x=0, 0.3, 0.5, 0.8 and 1 using electrochemical and surface physical techniques. The electrochemical behaviour was mainly determined by the Ir component for x<0.5. XPS show no change in surface composition during O<sub>2</sub> evolution. Band mixing may occur, causing a shift in oxidation potentials. The RuO<sub>2</sub> activity is lost, but the stability of the slightly activated IrO<sub>2</sub> is maintained.

### Electrooxidation of Urea at the Ruthenium Titanium Oxide Electrode

J. C. WRIGHT, A. S. MICHAELS and A. J. APPELBY, *AIChE J.*, 1986, **32**, (9), 1450-1458

The electrochemistry of urea at a Ru-Ti oxide electrode was investigated for aqueous solution concentrations of urea and chloride which are found in artificial kidney dialysate. Urea adsorbs on the electrode, depressing the observed current. For artificial kidney dialysate concentrations of urea and NaCl (0.50kg/m<sup>3</sup> and 100mol/m<sup>3</sup>, respectively) the major electrolysis products are N<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub> and the reaction mechanism is solution oxidation of urea by anodically generated Cl<sub>2</sub>. A N<sub>2</sub> yielding direct electrode reaction is observed at high urea concentrations (30kg/m<sup>3</sup>) and low NaCl concentrations (10-100mol/m<sup>3</sup>).

### Electrocatalytic Synthesis of Methyl Formate and Methylal from Methanol on a Platinum-Bonded Solid Polymer Electrolyte Membrane

K. OTSUKA and I. YAMANAKA, *Appl. Catal.*, 1986, **26**, (1-2), 401-404

The synthesis of methyl formate and methylal from CH<sub>3</sub>OH using a Pt-SPE membrane without any solvent, electrolyte or a divided cell is discussed. The electrochemical oxidation of methanol usually yields formaldehyde, formic acid or CO<sub>2</sub>. The rates of product formation and their selectivities can be controlled by the voltage between the Pt/SPE electrodes.

## PHOTOCONVERSION

### Bipolar TiO<sub>2</sub>/Pt Semiconductor Photoelectrodes and Multielectrode Arrays for Unassisted Photocyclic Water Splitting

E. S. MOTKIN, A. J. BARD, A. CAMPION, M. A. FOX, T. MALLOUK, S. E. WEBBER and J. M. WHITE, *J. Phys. Chem.*, 1986, **90**, (19), 4604-4607

Bipolar Pt/TiO<sub>2</sub> photoelectrodes, have been made from a polycrystalline TiO<sub>2</sub> film with sputter-deposited Pt. The photoelectrodes were assembled into multipanel arrays and vectorial charge transfer was observed. Several different multielectrode cells, using KOH and O<sub>2</sub> electrolytes, were constructed. In series configuration, the open-circuit voltage V<sub>oc</sub> is proportional to the number of panels used. With 5 panels in series V<sub>oc</sub>>3.6V is obtained, allowing unassisted photolytic (Xe lamp) water splitting.

### Efficient Homogeneous Photochemical Hydrogen Generators using Rhodium Compounds as Catalyst Precursors

H. HUKKANEN and T. T. PAKKANEN, *J. Mol. Catal.*, 1986, **37**, (2-3), 297-307

A homogeneous catalytic system is described which efficiently generates H<sub>2</sub> by visible light, using Ru(bipy)<sub>3</sub>Cl<sub>2</sub> as a photosensitiser, Rh carbonyls as catalysts and triethanolamine as an electron donor. The system is highly active only in organic medium.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Photoassisted Platinum Deposition on TiO<sub>2</sub> Powder Using Various Platinum Complexes

J.-M. HERRMANN, J. DISDIER and P. PICHAT, *J. Phys. Chem.*, 1986, **90**, (22), 6028-6034

Factors affecting the photoassisted deposition of Pt on powder TiO<sub>2</sub> have been examined in aqueous solutions containing different complexes. The deposition rate was identical for chloroplatinic acid, Na chloroplatinate and hexahydroxyplatonic acid, to a detection limit of 1ppm. TEM shows Pt deposits 1nm diameter on all the TiO<sub>2</sub> particles. Longer illumination and higher loadings give large agglomerates. Pd, Ag, Rh, Ir and Au have been deposited on TiO<sub>2</sub>.

## LABORATORY APPARATUS AND TECHNIQUE

### Stabilization of Misfet Hydrogen Sensors

S.-Y. CHOI, K. TAKAHASHI, M. ESASHI and T. MATSUO, *Sens. Actuators*, 1986, **9**, (4), 353-361

The drift in Pd-gate MOS sensors for H<sub>2</sub> detection can be eliminated by using Pd/Pt H<sub>2</sub> sensing gate and Ag/Cu/Pd/Pt reference gate differential-type sensors.

### A Glucose Sensor Based on the Adsorption of Glucose on a Palladium/Gold Modified Carbon Electrode

L. GORTON and G. JÖNSSON, *J. Mol. Catal.*, 1986, **38**, (1-2), 157-159

A Pd/Au-modified electrode for detecting glucose, based on the strong adsorption of glucose oxidase is reported. The electrode allows an extended potential range to be used for examination of potential behaviour and stability of immobilised oxidase.

## HETEROGENEOUS CATALYSIS

### Coke Formation on Platinum Metals Studied by Auger Electron Spectroscopy and Secondary Ion Mass Spectroscopy

J. W. NIEMANTSVERDRIET and A. D. VAN LANGEVELD, *Fuel*, 1986, **65**, (10), 1396-1399

Various techniques were used to distinguish between four types of carbonaceous deposits which may be present on a catalyst: molecular, carbidic, amorphous and graphitic C. Differences between Pt, Rh and Ir for C deposition from C<sub>2</sub>H<sub>4</sub> are discussed.

### Use of Noble Metals in Automobile Exhaust Catalysts

J. T. KUMMER, *J. Phys. Chem.*, 1986, **90**, (20), 4747-4752

A review of laboratory work on catalytic reactions for automobile exhaust purification is presented. Pt, Pd and Rh catalysts, oxidation of CO and hydrocarbons, NO reduction and the water-gas shift and steam-reforming reactions are examined. Literature indicating alloy formation between noble metals to be detrimental to catalysis, and segregation beneficial to catalysis is included. (117 Refs.)

### Sulphur-Induced Faceting of Platinum Catalyst Particles

P. J. F. HARRIS, *Nature*, 1986, **323**, (6091), 792-794  
S poisoning experiments on thin self-supporting Pt/Al<sub>2</sub>O<sub>3</sub> catalyst films were examined by TEM. S adsorption produced a change in morphology involving the formation of sharp (100) facets. The TEM's of unpoisoned Pt indicated well rounded particles with only light faceting and no sharp edges.

### NO Reduction by CO over Noble-Metal Catalysts under Cycled Feedstreams

H. MURAKI and Y. FUJITANI, *Ind. Eng. Chem., Prod. Res. Dev.*, 1986, **25**, (3), 414-419

The reduction of NO with CO was studied over  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supported Pt, Pd, Rh, Ru and Ir catalysts. The activities were measured using cycled feeds and steady non-cycled feeds. The catalyst activity was Rh>Ru>Ir>Pd>Pt. Under cycled feeding the activities of Pt and Pd were greater, the cycling affected Pt more than Pd. The order of periodic operation corresponded to susceptibility for CO self-poisoning.

### **Exhaust-Catalyst Development for Methanol-Fueled Vehicles: I.A Comparative Study of Methanol Oxidation over Alumina-Supported Catalysts Containing Group 9, 10 and 11 Metals**

R. W. MCCABE and P. J. MITCHELL, *Appl. Catal.*, 1986, 27, (1), 83-98

Catalysts to be used for the efficient oxidation of exhaust products from methanol fuelled vehicles were investigated. Highly dispersed Pt, Pd, Rh, Ag and Cu-Cr on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were tested. Pt and Pd oxidised methanol rapidly in the absence of CO and produced methyl formate below ~400K. With CO present methanol oxidation is strongly inhibited. Rh had much lower activity than Pt or Pd but was not much affected by CO.

### **Catalytic Wood Liquefaction Using a Hydrogen Donor Solvent**

P. E. ARAYA, S. E. DROGUETT, H. J. NEUBURG and R. BADILLA-OHLBAUM, *Can. J. Chem. Eng.*, 1986, 64, (5), 775-780

The direct wood liquefaction of pine sawdust in a H donor solvent was studied using Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Co-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Raney nickel catalysts and uncatyalsed runs at 673K and a pressure of 10MPa. The weight ratio of solvent:solid loaded was 2:1, the gas phase being either N<sub>2</sub> or H<sub>2</sub>. There was a high conversion to liquid and gaseous products. Liquefaction occurred under H<sub>2</sub> or N<sub>2</sub> with and without catalyst. Higher organic liquid production is favoured under H<sub>2</sub> in the presence of Pt and Co-Mo catalyst.

### **Atomic Structure of Ultrafine Catalyst Particles Resolved with a 200-keV Transmission Electron Microscope**

D. A. JEFFERSON, J. M. THOMAS, G. R. MILLWARD, K. TSUNO, A. HARRIMAN and R. D. BRYDSON, *Nature*, 1986, 323, (6087), 428-431

Results of investigations on the ultrastructures of very fine particles using a modified commercial 200keV TEM are presented. A new side-entry specimen stage in the microscope allows atomic arrays to be investigated. Catalysts examined included Pt/C and Pt colloidal sols, the sol particles were crystalline, with considerable surface roughness.

### **Dehydrogenation of Methylcyclohexene on a PtNaY Catalyst. Study of Kinetics and Deactivation**

J. F. GARCÍA DE LA BANDA, A. CORMA and F. V. MELO, *Appl. Catal.*, 1986, 26, (1-2), 103-121

The kinetics of the dehydrogenation of methylcyclohexene to toluene on a Pt/NaY zeolite and the deactivation of the catalyst have been studied. By comparing dehydrogenation rates for methylcyclohexane and methylcyclohexene it has been found with this catalyst that the slowest step in the overall dehydrogenation is the dehydrogenation of methylcyclohexane to methylcyclohexene, followed by the desorption of toluene from the metal.

### **The Effect of Various Bimetallics on the Graphite-Steam Reaction**

R. T. K. BAKER, J. A. DUMESIC and J. J. CHLUDZINSKI, *J. Catal.*, 1986, 101, (1), 169-177

Bifunctional Ni-Pt, Pt-Ti, Ni-Ru and Ni-Ti catalysts were studied for the C-steam reaction. One component increases the O reactivity and the other accelerates the supply of C from the source material to the catalyst-gas interface. The bimetallic systems exhibit a rate of catalytic attack of graphite in steam that is higher than the single components. Introducing a second metal can produce changes in the wetting characteristics of the catalyst on graphite.

### **Heterogeneous Catalytic Hydrogenation of Carola Oil Using Palladium**

N. HSU, L. L. DIOSADY, N. F. GRAYDON and L. J. RUBIN, *J. Am. Oil Chem. Soc.*, 1986, 63, (8), 1036-1042

The hydrogenation of carola oil was studied using Pd black, and compared with a Ni catalyst, for producing partially hydrogenated fats with low trans-isomer content. Pressure had the largest effect on trans-isomer formation. A maximum of 18.7% trans-isomer could be obtained, while Ni produces about 50% trans-isomer. At 250 psig and 50°C 5% Pd/C had twice the activity of Pd black. The oil samples contained ~1ppm Pd residue after filtration. Pd can be used at 50-150 times lower concentration than Ni.

### **A New Class of Catalysts: Palladium Supported on Phosphinated Inorganic Oxides**

R. L. AUGUSTINE and L. JIWAN, *J. Mol. Catal.*, 1986, 37, (2-3), 189-200

Modification of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub>-MgO by the attachment of pendant organophosphines gave phosphinated oxides which on treatment with Na<sub>2</sub>PdCl<sub>4</sub> and heating gave black, catalytically active species which are metallic Pd supported on these modified oxides. The pendant phosphine groups interact with the Pd metal to influence the olefin hydrogenation activity and to markedly decrease the double bond isomerisation capability of these catalysts.

### **Experiments on Heterogenization of Homogeneous Rhodium Catalysts, Illustrated for the Synthesis of Acetic Anhydride**

G. RITTER and G. LUFT, *Chem. Ing. Tech.*, 1986, 58, (8), 668-669

An attempt to combine the advantages of homogeneous co-ordinate catalysts and heterogeneous catalysts to produce a solid phase catalyst is discussed for Rh. Supports studied included SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, MgO/Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, and the effects of pressure and temperature for acetic anhydride syntheses were examined. The highest activity occurred for Rh on Al<sub>2</sub>O<sub>3</sub> or on Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> with  $\beta$ -diphenylphosphinoethylbiethoxysilane as fixative.

### Effects of the Variation of Electric Properties of TiO<sub>2</sub> Support on the Hydrogenation of CO and CO<sub>2</sub> over Rh Catalyst

I. TOMBÁČZ, J. KOSZTA and F. SOLYMOŠI, *Magy. Kem. Foly.*, 1986, **92**, (8), 373-380

The electrical properties of a TiO<sub>2</sub> support were altered by doping with cations, and the effects on the catalytic activity of Rh during hydrogenation of CO and CO<sub>2</sub> were investigated. Changing the electrical conductivity of TiO<sub>2</sub> affects the catalytic nature of Rh. Incorporating W<sup>6+</sup> ions which increased the electrical conductivity 1-2 orders of magnitude increased the turnover frequency of CH<sub>4</sub> formation. Mg<sup>2+</sup> and Al<sup>3+</sup> hardly affected the electrical conductivity or the activity of Rh.

### Direct Synthesis of Acetic Acid from Synthesis Gas over Rh-Mn-Zr-Li/SiO<sub>2</sub> Catalyst

T. NAKAJO, K.-I. SANO, S. MATSUHIRA and H. ARAKAWA, *Chem. Lett. Jpn.*, 1986, (9), 1557-1566

The direct synthesis of acetic acid from syngas has been investigated. Acetic acid was produced with > 63% selectivity over Rh-Mn-Zr-Li/SiO<sub>2</sub> catalyst at 300°C under a pressure of 100kg/cm<sup>2</sup> of syngas with a flow ratio CO:H<sub>2</sub>=9:1.

### Hydrogenolysis of Propane, n-Butane and Isobutane over Various Pretreated Ru/TiO<sub>2</sub> Catalysts

G. C. BOND, R. R. RAJARAM and R. BURCH, *J. Phys. Chem.*, 1986, **90**, (20), 4877-4887

The hydrogenolyses of the title compounds were investigated over Ru/TiO<sub>2</sub> containing 0.5 and 5 wt.%Ru, pretreated in various ways. Oxidation at 623K after a first reduction at 758K or 893K, followed by mild reduction, gives high-activity catalysts free of Cl<sup>-</sup> in a non-SMSI state. The highly dispersed Ru particles have CH<sub>4</sub> selectivities, and for n-butane the oxidised catalysts have a marked preference for terminal C-C bond breakage. Low activity catalysts were also produced.

### Chemisorption and Catalysis by Metal Clusters

R. B. MOYES, P. B. WELLS, S. D. JACKSON and R. WHYMAN, *J. Chem. Soc., Faraday Trans. I*, 1986, **82**, (9), 2719-2727

The properties of clusters derived from Ru(CO)<sub>12</sub> and H<sub>2</sub>Ru<sub>4</sub>(CO)<sub>12</sub> supported on SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> are discussed. The clusters are stable and give highly reproducible activity for ethene hydrogenation and ethane hydrogenolysis. Catalysts freshly prepared are initially in a non-steady state, pass through a maximum in activity, then decline to a steady-state value. Hydrocarbons are retained in the non-steady and steady states. Steady-state catalysts had low activity for ethene hydrogenation. Ru cluster catalysts show lower specific activity than corresponding Os catalysts.

### Ruthenium Tetroxide Catalysed Oxidation of Coals. The Formation of Aliphatic and Benzene Carboxylic Acids

L. M. STOCK and S.-H. WANG, *Fuel*, 1986, **65**, (11), 1552-1562

RuO<sub>4</sub> was used as a reagent for the oxidation of several different coals. Significant quantities of aliphatic, di-, tri- and tetracarboxylic acids, benzene, di-, tri-, tetra-, and pentacarboxylic acids were produced in these oxidation reactions, and more than 100 products have been identified. A large number of carboxylic acids were formed in this reaction which selectively preserves the aliphatic portion of the coal.

## HOMOGENEOUS CATALYSIS

### "Counter" Phase Transfer Catalysis by Water-Soluble Phosphine Complexes. Catalytic Reduction of Allyl Chlorides and Acetates with Sodium Formate in Two-Phase Systems

T. OKANO, Y. MORIYAMA, H. KONISHI and J. KIJI, *Chem. Lett. Jpn.*, 1986, (9), 1463-1466

In the reduction of allyl chlorides and acetates with Na formate in a heptane-water two-phase system, water soluble Pd complexes function as a novel type of catalyst which transports the substrate into the aqueous phase and causes it to react with Na formate.

### Colloidal Palladium Supported on Chelate Resin Containing Iminodiacetic Acid Groups as Hydrogenation Catalysts

H. F. HIRAL, S. KOMATSUZAKI and N. TOSHIMA, *J. Macromol. Sci.-Chem.*, 1986, **A23**, (8), 933-954

Colloidal catalyst Pd/chelate resin containing iminodiacetic acid was prepared, and cyclopentadiene was hydrogenated to cyclopentene in 97.1% selectivity at 100% conversion of cyclopentadiene under 1atm H<sub>2</sub> in CH<sub>3</sub>OH at 30°C. The finely dispersed Pd particles were 10-60Å in diameter. X-ray microanalysis and elution analysis showed the existence of large amounts of Pd ion complexes in the resin. Pd metal in the resin was ~5% of the total Pd. Since the resin after removal of most of the ionic Pd had almost the same catalytic activity as before, it was concluded that the finely dispersed Pd particles are the active species in the catalyst.

### Oxidation of Alcohols by Transfer of Hydrogen in the Presence of Saturated Ketones. Application of the Selectivity of Catalyst Transfer by RhH(PPh<sub>3</sub>)<sub>4</sub>

D. BEAUPERE, M. MASSOUI, R. RALAINIRINA and R. UZAN, *Nouv. J. Chim.*, 1986, **10**, (8/9), 493-498

A kinetic study of the oxidation of alcohols by H transfer using RhH(PPh<sub>3</sub>)<sub>4</sub> as catalyst and ketone as H acceptor has been performed under mild conditions. Prochiral enones were reduced by the H, with an enantiomeric excess reaching 52%.

## FUEL CELLS

### Performance Study of a Fuel Cell Pt-on-C Anode in Presence of CO and CO<sub>2</sub>, and Calculation of Adsorption Parameters for CO Poisoning

H. P. DHAR, L. G. CHRISTNER, A. K. KUSH and H. C. MARU, *J. Electrochem. Soc.*, 1986, **133**, (8), 1574-1582

The behaviour of a 0.4mg/cm<sup>2</sup> porous Pt/C fuel cell anode with electrochemically active surface area of 150m<sup>2</sup>/g of Pt was measured to find polarisation losses due to CO<sub>2</sub> and CO in the H<sub>2</sub> fuel. The anode was tested as a floating electrode in a half-cell assembly in the presence of 100 wt.% H<sub>3</sub>PO<sub>4</sub> at 190°C. Among conclusions reached are that the combined voltage loss for dilution by CO and CO<sub>2</sub>, and poisoning by CO is the sum of the dilution and poisoning voltage losses.

### Glycol/Air Fuel Cells

R.-Z. QIU, *Int. J. Hydrogen Energy*, 1986, **11**, (12), 817-820

The development of a glycol/air fuel cell is discussed. The electrode catalyst made of Pt:Pd:Bi = 3:2:1 on active C as carrier was very effective for the electrochemical oxidation of glycol in KOH solution at room temperature. The loading of Pt-Pd can be as low as 1mg/cm<sup>2</sup>. A 2W battery consisting of 10 cells with a capacity of 1000Ah has been constructed.

## CORROSION PROTECTION

### Atmospheric Corrosion Test on Pd/Ag-Thick Film Lead Paths

A. H. C. HENDRIKS, *Metall.*, 1986, **40**, (10), 1018-1021

The effects of corrosive gases on the solderability of Pd-Ag thick film lead paths were examined. Tests simulating atmospheres containing strongly corrosive industrial pollutant gases of SO<sub>2</sub>, H<sub>2</sub>S, NO<sub>2</sub>, O<sub>3</sub> and Cl<sub>2</sub> separately, or in different combinations were performed on different Pd-Ag thick film lead paths for 14 days. H<sub>2</sub>S was the only one to have a bad effect.

## TEMPERATURE MEASUREMENT

### Platinum-Point Reference in the Calibration of the Visual Disappearing-Filament Optical Pyrometer

D. DAS and M. S. CHANDRASEKHARAIHAH, *High Temp. Sci.*, 1986, **21**, (3), 161-168

For measuring the brightness temperatures above 1500°C the visual disappearing-filament optical pyrometer needs its range scales to be calibrated before every use; therefore a modified procedure uses a Pt-point reference to reduce the work of calibration without losing precision or accuracy.

### Automated Platinum Resistance Thermometer for Determining the Composition of Salt Solutions and Purity of TNT

J. M. C. RIDDEN, *J. Hazardous Mater.*, 1986, **13**, (3), 329-336

A Pt resistance thermometer coupled to a bridge circuit has been used for determining the solidification point of TNT and the crystallising point of certain aqueous salt solutions. The system can be automated.

### Thin-Film Platinum Resistance Thermometer for Use at Low Temperatures and in High Magnetic Fields

T. HARUYAMA and R. YOSHIZAKI, *Cryogenics*, 1986, **26**, (10), 536-538

A thin film commercially available Pt resistance thermometer was examined for thermometry from 20-300K in high magnetic fields up to 5T. It was found that the thermometer was precise to ± 0.1K within this range. The magnetoresistance of the Pt resistance thermometer at 30K is ~1.5% for a magnetic field of 5T.

### Resistance Thermometer of Rhodium-Ferrum Microwire

S. P. LOGVINENKO and G. F. MIKHINA, *Cryogenics*, 1986, **26**, (8), 484-485

Resistance thermometers based on glass insulated cast microwire of Rh-0.5at.%Fe have been examined. The alloy cast as a microwire has the same temperature dependence of resistivity as the alloy prepared by the powder metallurgical method. The thermometer has a high relative sensitivity in the low temperature region, ~15%/K at 1.5K.

### Thick Film Chip Resistors for Use as Low Temperature Thermometers

Q. LI, C. H. WATSON, R. G. GOODRICH, D. G. HAASE and H. LUKEFAHR, *Cryogenics*, 1986, **26**, (8), 467-470

The resistance and magnetoresistance of a commercially produced Bi<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub> thick film resistor have been measured from 80K-15mK in fields up to 20T. Between 2.5 and 0.1K the resistance of a 1kΩ resistor fits  $R = A \exp(B/T^{\alpha})$ .

## MEDICAL USES

### Study on Interaction of Antitumor Active Platinum(II) Complexes with DNA and Its Constituents by Means of High-Performance Liquid Chromatography

K. INAGAKI and Y. KIDANI, *Nippon Kagaku Kaishi*, 1986, (7), 1025-1031

Selective binding of anti-tumour Pt(II) complexes with DNA was studied by enzymatic digestion and liquid chromatography. Adjacent guanine bases were the preferred Pt binding sites in DNA. Reaction products of d(GpG) with a variety of anti-tumour Pt complexes were separated and examined.