

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Thermodynamics of the Systems of the Platinum Metals with Other Transition Metals: I. Integral Data

H. KLEYKAMP, *J. Nucl. Mater.*, 1993, 201, 193–217

A review is presented of various correlated thermodynamic parameters of around 190 intermetallic compounds of the platinum group metals with transition metals, in order to expand information about the intermetallic compounds formed with the fission products, fuel and claddings by the Pt metals after irradiation of nuclear fuels. Data presented include: entropies and enthalpies of formation, Gibbs energies of formation as a function of temperature, excess electronic entropies of formation and lattice contractions. (124 Refs.)

Adsorption and Decomposition of 2-Chloroethyl Ethyl Sulfide on Pt(111): A Temperature Programmed Desorption and Laser-Induced Thermal Desorption/Fourier Transform Mass Spectrometry Study

X.-L. ZHOU, Z.-J. SUN and J. M. WHITE, *J. Vac. Sci. Technol. A*, 1993, 11, (4), 2110–2116

The adsorption and decomposition of 2-chloroethyl ethyl sulphide (CEES), a simulant of mustard gas, was examined by various techniques on Pt(111). At 90 K sulphide adsorption through the S atom to Pt is molecular and very strong. Molecular CEES desorption only occurs at high coverages, > 50% saturation of the first monolayer, and peaks at 180 K for physisorbed and at 220–380 K for chemisorbed. Only 15% of the monolayer desorbs molecularly. The chemisorbed submonolayer, CEES, dissociates at 280–380 K giving H₂, HCl and C₂H₄, surface S and CCH₃ at low coverages and also C₂H₆ and S(C₂H₅)₂ at high coverages. CCH₃ decomposes, to H₂ at 450–700 K, and the remaining surface C and S poison the surface for further sulphide decomposition.

Magnetic Anisotropy and Lattice Strain in Co/Pt Multilayers

B. ZHANG, K. M. KRISHNAN, C. H. LEE and R. F. C. FARROW, *J. Appl. Phys.*, 1993, 73, (10), 6198–6200

The correlation is reported between perpendicular anisotropy and in-plane lattice strain in Co/Pt multilayers having varying thicknesses of Co and Pt layers, by using the polar magneto-optic Kerr effect and transmission electron microscopy. The largest perpendicular anisotropy and square hysteresis loop occurred when the thickness of the Co layers was 3 Å while the Pt layers were subjected to ~-2% in-plane strain. It is suggested that the magnetoelastic or stress anisotropy is important in inducing perpendicular anisotropy in these multilayer magnetic films.

Preparation and Characterization of Platinum-Ceramic Composite Powders and Thin Films

K. KOHNO, Y. TAKEDA, N. IMANISHI, Y. SAKAKI, K. SAKAMOTO and O. YAMAMOTO, *J. Am. Ceram. Soc.*, 1993, 76, (1), 192–196

Pt-ceramic (TiO₂, ZrO₂ and ZrO₂-5 mol% Y₂O₃ (PSZ)) composite powders were prepared by a sol-gel-like liquid-phase reaction. The sintered films of the powders were good metallic conductors; at room temperature the resistivity of the Pt-PSZ film was ~1.5 × 10⁻⁵ Ω cm which is almost comparable to that of pure Pt (1.05 × 10⁻⁵ Ω cm). The films also exhibited excellent cathodic O reduction, giving an overpotential for the O reduction of < 20 mV at 750°C even at a high current density of 0.1 A/cm².

Clustering of Platinum Atoms into Nanoscale Particle and Network on NaY Zeolite

R. RYOO, S. J. CHO, C. PAK and J. Y. LEE, *Catal. Lett.*, 1993, 20, (1,2), 107–115

Pt atoms were supported on NaY zeolite by ion exchange of Pt(NH₃)₄²⁺. Pt was clustered into a 1 nm cluster, and quantum-size wire 3 nm in diameter was formed into three dimensional networks of > 100 nm resulting from the reduction of the Pt species, were studied by EXAFS, TEM and Xe-adsorption measurements. The Pt network appears not to damage the framework of the zeolite.

Preparation and Characterization of Colloidal Silver-Platinum Alloys

K. TORIGOE, Y. NAKAJIMA and K. ESUMI, *J. Phys. Chem.*, 1993, 97, (31), 8304–8309

Colloidal Ag-Pt alloys were prepared by NaBH₄ reduction of (Ag₂[Pt(C₂O₄)₂]) (1) in ethylene glycol and characterised. The metal particle had homogeneous {111} lattice spacing of 2.31 ± 0.02 Å, which indicates that they are Ag-Pt alloys. The alloy formation was studied by step-by-step reduction of (1).

Fabrication of High Aspect Ratio Silicon Pillars of < 10 nm Diameter

W. CHEN and H. AHMED, *Appl. Phys. Lett.*, 1993, 63, (8), 1116–1118

Uniform high aspect ratio 5–7 nm structures in the form of Si nanopillars with aspect ratio of height to diameter of ~7:1, the smallest to date, have been fabricated without the use of chemical etching. Thus the probability of Si-O-H compounds formation is reduced. The technique combined ultrasonic agitation during development, a lift-off mask of AuPd film deposited by ionised beam deposition and reactive ion etching. The dimensions of the sub-10 nm pillars are similar to the crystalline structures in porous Si.

Phase Diagram of the Ir-Sb System on the Antimony-Rich Part

T. CAILLAT, A. BORSHCHEVSKY and J.-P. FLEURIAL, *J. Alloys Compd.*, 1993, **199**, (1-2), 207-210

A reinvestigation of the Ir-Sb system in the range 50-100 at.% Sb has confirmed the existence of three compounds: IrSb, and IrSb₂, formed by peritectic reactions at 1141°C and 1475 ± 30°C, respectively, and IrSb which melts congruently at 1645 ± 25°C. IrSb₂ formed a degenerate eutectic with Sb at 621°C.

Effect of the Deposition Temperature on the Iridium Film Microstructure Produced by Metal-Organic Chemical Vapour Deposition: Sample Characterization Using X-Ray Techniques

N. V. GELFOND, F. V. TUZIKOV and I. K. IGUMENOV, *Thin Solid Films*, 1993, **227**, (2), 144-152

Thin Ir films were obtained by MOCVD via the pyrolysis of Ir tris(acetylacetonate) on glass and quartz at atmospheric pressure with added H₂ at 370-550°C. Only the crystal phase of metal Ir was found. Particles were either "compact" (axial ratio no lower than 1:3) or "flattened-out" (disks, cracks, plates and shells) particles. The mean thickness of the "flattened-out" particles increased with increasing substrate temperature from 370 to 470°C, and the maximum volume share of these particles was seen in the 420-470°C deposition range. An increase or decrease in substrate temperature in MOCVD processes leads to almost complete disappearance of the particles of this shape.

Interactions in the System PbO-B₂O₃-RuO₂ at Temperatures to 1473 K

N. S. LOZINSKII and V. G. CHEKHOVSKII, *Zh. Prikl. Khim. (Russ.)*, 1993, **66**, (3), 486-491

Thermal treatment of the furnace charge mixture containing PbO, B₂O₃ and RuO₂ was performed at ≤ 973 K. Chemical interaction at 973 K resulted in the formation of Pb₂Ru₂O_{7-x}, which further reacted with Pb containing solutions at higher temperature forming RuO₂. At the same temperature of treatment, there was a tendency towards a decrease in the ratio between Pb₂Ru₂O_{7-x} : RuO₂ phases with a decrease in the molar ratio of PbO : B₂O₃ in the material composition.

Critical Behaviour of the Magnetoresistance of NdRu₂Si₂ Near the Néel Point

M. A. SALGUEIRO, B. G. ALMEIDA, M. M. AMADO, J. B. SOUSA, B. CHEVALIER and J. ÉTOURNEAU, *J. Magn. & Magn. Mater.*, 1993, **125**, (1-2), 103-109

The temperature and applied magnetic field dependencies of the magnetoresistance of the strongly anisotropic NdRu₂Si₂ antiferromagnet, were studied for temperatures near the Néel point. Data were analysed in terms of the available theoretical models describing the effect of the critical spin fluctuations on the magnetoresistance near T_N.

Spin Glass Behaviour of the Perovskite-Related Compounds, Sr_nLaCuRuO_{n+5} (n = 1,2,3)

S. H. KIM and P. D. BATTLE, *J. Magn. & Magn. Mater.*, 1993, **123**, (3), 273-282

The magnetic properties of the title compounds were studied by DC susceptibility measurements at 6 K ≤ T ≤ 300 K. SrLaCuRuO₆ had a simple orthorhombic perovskite structure whereas Sr₂LaCuRuO₈ and Sr₃LaCuRuO₈ adopted the 2D K₂NiF₄ and the intermediate Ruddlesden-Popper structures. At low temperatures the DC susceptibility data showed sharp cusps and a divergence between the zero-field-cooled and field-cooled susceptibilities, characteristic of spin-glass behaviour.

CHEMICAL COMPOUNDS

A Convenient Preparation of Dinuclear Pt(II) Phosphine Complexes

W. BARATTA and P. S. PREGOSIN, *Inorg. Chim. Acta*, 1993, **209**, (1), 85-87

A simple one-step method for the preparation of dinuclear chloro-bridged Pt(II) phosphine complexes, [Pt(μ-Cl)Cl(PR₃)₂]₂, is reported. The synthesis is carried out in *p*-chlorotoluene and the preparation of tertiary phosphines: PMe₂Ph, P(*p*-Tol)₃, PPh₃, PBu₃ and PEt₃ is described.

A New Cross-Linkable Palladium(0) Complex and Its Use for Electroless Metalization of Epoxy Resins

B. TIEKE and A. ZAHIR, *Chem. Mater.*, 1993, **5**, (6), 891-897

A new cross-linkable Pd(0) complex tris(4,4'-(2,3-epoxypropoxy)dibenzylideneacetone)Pd(0) (1) has been prepared. The mixture of (1) with the diglycidyl ether of bisphenol A can be cured with various epoxy hardeners to yield a 3-dimensional polymer network. The presence of (1) in the resins does not affect mechanical strength, electrical and thermal conductivity, but changes thermal stability and chemical properties. Upon annealing at > 150°C the complex is decomposed to a fine dispersion of highly catalytic 5-20 nm diameter Pd particles in the resin matrix.

Tetra- and Hexanuclear Iridium Clusters in NaY Zeolite: Characterization by Infrared Spectroscopy

T. BEUTEL, S. KAWI, S. K. PURNELL, H. KNÖZINGER and B. C. GATES, *J. Phys. Chem.*, 1993, **97**, (28), 7284-7289

Molecular Ir carbonyl clusters, [Ir₄(CO)₁₂] and [Ir₆(CO)₁₆] were prepared from [Ir(CO)₂(acac)] in the cages of NaY zeolite in the presence of CO. The clusters and their reversible decarbonylation and recarbonylation were characterised by IR spectroscopy at -196 to 300°C. The spectra showed the formation of identical structures as those formed by recarbonylation of decarbonylated [Ir₄(CO)₁₂]. The results give the first evidence of intermediates in a reversible metal carbonyl cluster formation.

Mg₃RuH₆, a Complex Hydride Containing Two Types of Hydrogen Atoms Differing in Their Bonding

W. BRONGER, K. JANSEN and G. AUFFERMANN, *J. Alloys Compd.*, 1993, **199**, (1-2), 47-51

A new ternary ruthenium hydride, Mn₃RuH₆, has been successfully prepared and the structure determined. The complex crystallises in the orthorhombic space group *Cmcm*. The atomic arrangement contains two differently bonded types of hydrogen atoms, one forms complex Ru-H anions, the other is surrounded by Mg cations.

ELECTROCHEMISTRY

The Unusual Reduction Behavior of Thin, Hydrated Platinum Oxide Films

V. I. BIRSS and M. GOLEDZINOWSKI, *J. Electroanal. Chem.*, 1993, **351**, (1 and 2), 227-243

Thin hydrated β -Pt oxide films were formed electrochemically by rapid potential cycling in 0.5 M H₂SO₄. The oxides could be potentiostatically reduced at potentials as high as 0.65 V vs. RHE. After partial film reduction at constant potentials 0.65-0.3 V, sweep reduction of the remaining oxide showed that significant changes had occurred in the films. Up to 20% more charge is passed than when the film is reduced exclusively in a potential sweep. The potential and shape of the remaining β -oxide peak was much altered after partial potentiostatic reduction.

Anodic Behaviour of Platinum Alloys with Nickel, Iron and Sulphur in Sulphuric Acid Solutions

S. A. SIMANOVA, V. I. BASHMAKOV, O. N. TROSHINA, V. A. BRYUKVIN, B. A. FISHMIN, N. V. PENSKII and E. D. DZHAVAKHADZE, *Zh. Prikl. Khim. (Russ.)*, 1993, **66**, (1), 27-30

Studies were performed of the electrochemical behaviour of alloys containing in wt.% 90Fe-10Pt (1), 90Ni-10Pt (2), 80Fe-10Pt-10S (3) in sulphuric acid solution containing 0.5 M Na₂SO₄ and 1.0 M H₂SO₄ in the potential range of -0.3 to +2.4 V, at 65°C. When anodic dissolution of (1) and (3) alloys was performed in sulphuric acid solution at potentials of \leq 2.2 V, Pt passed into the residue as metallic or oxide phases.

Studies of the Hydrogen Evolution Reaction on Lanthanum Phosphate-Bonded Composite Nickel-Ruthenium Electrodes in 1 M Alkaline Solutions

H. DUMONT, P. LOS, A. LASIA, H. MÈNARD and L. BROSSARD, *J. Appl. Electrochem.*, 1993, **23**, (7), 684-692

Studies of the electrocatalytic properties of La phosphate-bonded composite Ni-Ru electrodes for the H and O evolution reactions were performed in 1 M KOH at 25°C. Ru was chemically deposited on Ni powder particles prior to polymerisation of Ni/Ru powder with La phosphate. The electrodes were very active for the HER over Ru contents of 0-10 wt.%.

APPARATUS AND TECHNIQUE

Novel Platinum-Tin Oxide-Silicon Nitride-Silicon Dioxide-Silicon Gas Sensing Component for Oxygen and Carbon Monoxide Gases at Low Temperature

W. P. KANG and C. K. KIM, *Appl. Phys. Lett.*, 1993, **63**, (3), 421-423

A Pt-SnO_x-Si₃N₄-SiO₂-Si-Al metal-insulator-semiconductor capacitor has been developed for sensing CO and O₂. The Pt provides preferential adsorption sites for O₂ and causes the adsorbed O₂ molecules to dissociate and spill over onto the SnO_x and enhance the chemisorptive and catalytic activities of the SnO_x for gas detection. The sensor can operate at room temperature and at much lower temperatures than conventional solid state gas detectors.

Enhanced Optical Detection of Hydrogen Using the Excitation of Surface Plasmons in Palladium

B. CHADWICK and M. GAL, *Appl. Surf. Sci.*, 1993, **68**, (1), 135-138

A novel method for the optical detection of H, based on the generation of surface plasmons at a Pd/dielectric interface is presented. Large (> 90%) changes in reflected light intensity from the sensor element were observed when the sensor was exposed to H concentrations corresponding to percentage levels. This represents a 10-fold increase of the reflectivity change observed in sensors using normal reflection from Pd. The technique is sensitive to low H concentrations.

Iridium Oxide-Based Microelectrochemical Transistors for pH Sensing

K. PÁSZTOR, A. SEKIGUCHI, N. SHIMO, N. KITAMURA and H. MASUHARA, *Sens. Actuators B*, 1993, **12**, (3), 225-230

Based on open-circuit potential measurements, the pH sensitivity of an anodic electrodeposition IrO₂ film on Au wire has been determined. The pH sensitivity showed good reproducibility between samples, and was independent of film oxidation state at -65 mV/pH. Microelectrochemical transistors based on IrO₂-Au wire electrodes and sensitive to pH have been successfully fabricated and characterised. The response time for a change in pH is < 40 s.

Improved Alcohol Biosensor Based on Ruthenium-Dispersed Carbon Paste Enzyme Electrodes

J. WANG, E. G. ROMERO and A. J. REVIEJO, *J. Electroanal. Chem.*, 1993, **353**, (1 and 2), 113-120

The use of Ru-dispersed graphite for greatly improving the performance of reagentless C paste biosensors for alcohol is demonstrated. The Ru centres were found to be integral parts of the graphite particles, thus eliminating dissolution (leakage) problems which are characteristic of mediator-based alcohol sensors. Ru-dispersed graphite showed a marked lowering of the overvoltage for the oxidation of liberated NADH.

Electrochemiluminescent Sensing for the Characterization of DNA-Interacting Antitumor and Antiviral Agents

Y. IKARIYAMA, Y. TAGUCHI, T. SUZAWA, E. KOBATAKE and M. AIZAWA, *Sens. Actuators B*, 1993, **14**, (1-3), 725-727

Electrochemiluminescence (ECL) of the Ru complex tris(1,10-phenanthroline)Ru(II) was used in a sensing probe for investigating the binding mode of DNA-binding antiviral or antitumor agents. In ECL-based typing of antiviral agents, the relative luminescence was determined by comparison with the luminescent value of the Ru complex in the free form, and in the presence of DNA, and DNA and antiviral agent. The intensity of the luminescence depends on the DNA-binding mode of each agent.

JOINING

Metal-Ceramic Interface Adhesion: Band Structure Calculations on Pt-NiO Couples

R. S. BOORSE, P. ALEMANY, J. M. BURLITCH and R. HOFFMANN, *Chem. Mater.*, 1993, **5**, (4), 459-464

Studies showed that under certain annealing conditions Pt-NiO couples form NiPt intermetallic layers at the interface which gives a 4-fold increase in the ultimate shear strength of the interface due to the inclusion of a 1 nm thick NiPt interlayer. This is caused by metal-O bonding at the interface. Extended Hückel calculations showed ~ 5-fold increase in adhesion energy in NiPt-NiO over Pt-NiO.

HETEROGENEOUS CATALYSIS

Behavior of Highly Dispersed Platinum Catalysts in Liquid-Phase Hydrogenations

M. A. GUTIÉRREZ-ORTIZ, J. A. GONZÁLEZ-MARCOS, M. P. GONZÁLEZ-MARCOS and J. R. GONZÁLEZ-VELASCO, *Ind. Eng. Chem. Res.*, 1993, **32**, (6), 1035-1040

A series of highly dispersed Pt catalysts supported on Al₂O₃ containing 0.5-3.0 wt.% Pt was prepared by adsorption from solution. The kinetic behaviour of the catalysts was studied during the liquid-phase hydrogenation of benzene in a stirred tank reactor. For a constant dispersion, a certain amount of surface Pt remained inactive, due either to inaccessibility of the reagents or to poisoning. When H pressure increased, the reaction order shifted from 1 to 0. The apparent activation energy was 72 kJ/mol.

Effect of Alkaline Earth Added to Platinum-Supporting Oxides on Platinum Dispersion and Dehydrogenation Activity

P. K. AHN, S. NISHIYAMA, S. TSURUYA and M. MASAI, *Appl. Catal. A: Gen.*, 1993, **101**, (2), 207-219

Studies of the modification of SiO₂ gel, silicalite and H-ZSM-5 supports by adding Mg, Ca, Sr and Ba, showed an increase in Pt dispersion, which caused an increase in the dehydrogenation activity of the catalysts. The modification by adding alkaline earth made the zero points of charge values shift to the basic region, from pH 1.7 to pH 11.1.

Catalytic Control of Diesel Engine Particulate Emission: Studies on Model Reactions over a EuroPt-1 (Pt/SiO₂) Catalyst

E. XUE, S. SESHAN, J. G. VAN OMMEN and J. R. H. ROSS, *Appl. Catal. B: Environ.*, 1993, **2**, (2-3), 183-197

Studies of the catalytic oxidation of NO to NO₂ in the presence of SO₂ over standard Pt/SiO₂ catalyst (EUROPT-1) showed that Pt/SiO₂ is very active during catalysis of both of NO + O₂ to NO₂ and of SO₂ + O₂ to SO₃. A significant effect of NO/NO₂ on SO₂ oxidation was observed, with complex species such as N_x-S_x-O_x being formed on the Pt surface.

Alkane Transformations on Supported Platinum Catalysts. Part 2: Reactions of Propane and of *n*-Butane on EUROPT-1 Modified by Titania and by Alumina

G. C. BOND and L. HUI, *J. Catal.*, 1993, **142**, (2), 512-530

Studies of EUROPT-1 6.3%Pt/SiO₂ catalyst modified by additions of TiO₂ and Al₂O₃ were performed during propane and *n*-butane reactions. Two types of pretreatment were used: high-temperature reduction (750 K) and then oxidation followed by low-temperature reduction (520 K). Addition of TiO₂ decreased the rates of all reactions, but with butane the isomerisation was selectively poisoned. When Al₂O₃ was added, the H:Pt ratio decreased but the rates of the alkane reactions decreased only slowly until attaining ~ 18 wt.% Al₂O₃ loading. Results are interpreted by a simple site-blocking model.

Electrochemical Modification of CH₃OH Oxidation Selectivity and Activity on a Pt Single-Pellet Catalytic Reactor

C. A. CAVALCA, G. LARSEN, C. G. VAYENAS and G. L. HALLER, *J. Phys. Chem.*, 1993, **97**, (23), 6115-6119

The catalytic activity and selectivity of Pt for CH₃OH oxidation to HCHO and CO₂ can be altered significantly and reversibly by depositing a Pt catalyst film on an Y₂O₃-stabilised ZrO₂ (YSZ) disc and by applying current or potential between the film and an Ag film on the other side of the O²⁻ conducting YSZ disc, which is held in a CH₃OH-O₂ mixture. The HCHO production rate was ~100 times higher than the rate of O²⁻ supply to the catalyst with a 2-fold increase in selectivity. This is a new NEMCA effect in a single pellet flow reactor.

Characterization of Pt-Sn Bimetallic Catalysts Supported on Alumina and Niobia

D. A. G. ARANDA, F. B. NORONHA, M. SCHMAL and F. B. PASSOS, *Appl. Catal. A: Gen.*, 1993, **100**, (1), 77-84

Bimetallic Pt-Sn catalysts supported on Al₂O₃ and Nb₂O₅ were characterised by TPR, H chemisorption and cyclohexane dehydrogenation. The TPR profiles of Nb₂O₅ supported Pt-Sn catalysts showed the presence of different precursors from those obtained on Al₂O₃. After reduction at 773 K, Pt/Nb₂O₅ catalysts displayed a strong metal-support interaction (SMSI) effect, leading to a lower H adsorption capacity of Pt, with the creation of new interfacial active sites.

Polymer-Protected Palladium-Platinum Bimetallic Clusters: Preparation, Catalytic Properties and Structural Considerations

N. TOSHIMA, T. YONEZAWA and K. KUSHIHASHI, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, (14), 2537-2543

Well dispersed, homogeneously sized, stable colloidal dispersions of polymer-protected Pd/Pt bimetallic clusters were produced by refluxing mixed solutions of PdCl₂ and H₂PtCl₆·6H₂O in 1:1 v/v EtOH/H₂O in the presence of poly(*N*-vinyl-2-pyrrolidone). Dispersions of the clusters were used as catalysts in the selective hydrogenation of cycloocta-1,3-diene to cyclooctene at 30°C under H₂ at atmospheric pressure. A Pd:Pt (4:1 mole ratio) bimetallic cluster was the most active catalyst, being twice as active as a typical colloidal Pd catalyst for diene hydrogenation. The most catalytically active cluster particle had a Pt core surrounded by Pd.

The Effect of Pretreatment of Pd-Rh Catalysts on Their Activity during Contamination by Mercury

T. M. GRISHINA, *Vestn. Mosk. Univ., Ser. Khim.*, 1993, **34**, (2), 181-184

Studies were performed of the effect of Hg poisoning on Pd-Rh catalysts which were either freshly prepared or artificially stabilised (aged). The catalysts which were aged displayed higher resistance to Hg poisoning than their freshly prepared analogues. The maximum resistance to Hg poisoning was shown by skeletal Rh and high content Rh alloy catalysts.

Catalysis of Hydrosilylation, Part XXII: Polymer-Protected Immobilized Platinum Complex Catalysts for Gas-Phase Hydrosilylation of Acetylene

B. MARCINIEC, Z. FOLTYNOWICZ and M. LEWANDOWSKI, *Appl. Organomet. Chem.*, 1993, **7**, (3), 207-212

A general method for immobilisation of a Pt catalyst prepared from complex H₂PtCl₆·6H₂O dissolved in EtOH, by anchoring via amine and mercapto groups to SiO₂, followed by formation of a polymer layer which protects the catalyst against leaching, is presented. The catalytic system obtained was very active, selective and stable during a long term hydrosilylation of acetylene by trichlorosilane in a gas-phase flow method.

Conversion under Hydrogen of Dichlorodifluoromethane over Supported Palladium Catalysts

B. COQ, J. M. COGNION, F. FIGUÉRAS and D. TOURNIGANT, *J. Catal.*, 1993, **141**, (1), 21-33

Studies of the conversion under H₂ of CF₂Cl₂ in the gas phase between 433-523 K over Pd black and Pd supported on Al₂O₃, graphite or AlF₃ showed the yields of two main products, CH₂F₂ and CH₄. The selectivity of the reaction slightly depended on the size of the Pd particles, with large particles favouring CH₂F₂ formation. However, the nature of the support affected the selectivity and with AlF₃ carrier, the highest selectivity of 81% was obtained in CF₂H₂.

Polymer-Supported Pd(II) Wacker-Type Catalysts. II. Application in the Oxidation of Dec-1-ene

H. G. TANG and D. C. SHERRINGTON, *J. Catal.*, 1993, **142**, (2), 540-551

A number of polymer-supported Pd(II) catalysts were prepared using polymers with nitrile(cyanomethyl) ligands, five of these used polybenzimidazole backbones, one a polystyrene skeleton and one a polyacrylonitrile backbone. The supported catalysts were used with CuCl₂ co-catalyst to oxidise dec-1-ene to methyl ketone under normal Wacker oxidation conditions. The most active Pd(II) species was one immobilised on a highly rigid *N*-cyanomethylated polybenzimidazole. The polymer-supported catalysts remained very active at ~120°C, without formation of Pd(0) black and without need for addition of HCl.

Growth of Ce on Rh, Surface Alloy Formation and the Preparation and Properties of Rh/Ceria Model Planar Catalysts

J. P. WARREN, X. ZHANG, J. E. T. ANDERSEN and R. M. LAMBERT, *Surf. Sci.*, 1993, **287/288**, Part A, 222-227

The deposition of Ce on Rh has been studied over a range of conditions. At room temperature Ce grows on Rh layer by layer, and annealing these films or depositing films at higher temperatures causes interdiffusion and the formation of a stable surface alloy, Ce₂Rh₂. Oxidising the Ce overlayers at room temperature forms a continuous oxide film, and heat treatment agglomerates the oxide film.

Supported Ternary Sulfide Phases: Characterization and Catalytic Properties of Alumina-Supported Ni_{1-x}Ru_xS₂

J. A. DE LOS REYES, M. VRINAT, C. GEANTET, M. BREYSSE and J. GRIMBLot, *J. Catal.*, 1993, **142**, (2), 455-464

A number of the solid solution sulphides Ni_{1-x}Ru_xS₂ supported over Al₂O₃, were prepared up to x = 0.7 by stepwise impregnations and further sulphidation. These phases are stable under test conditions showing a 30-fold increase in hydrogenation activity in comparison to pure Ru sulphide/Al₂O₃.

HOMOGENEOUS CATALYSIS

Platinum-Catalysed Enantioselective Hydroformylation of Styrene. Platinum-Diphosphine-Tin(II) Fluoride Catalytic System: A Novel Asymmetric Hydroformylation

L. KOLLÁR, T. KÉGL and J. BAKOS, *J. Organomet. Chem.*, 1993, **453**, (1), 155-158

Studies of the asymmetric hydroformylation of styrene with a number of preformed and "in situ" Pt catalysts under various conditions is presented. Sn(II) fluoride was used as co-catalyst, giving a catalytic system of unusually high stability. Absolute configuration of the 2-phenylpropanal which varied with the temperature used, was formed in the presence of the optically active 2,4-bis(diphenylphosphino)pentane.

Colloidal Palladium, Easily Formed in Organic Solvents, is a Highly Active and Stable Catalyst for Selective Hydrogenations and Dehydrohalogenations

L. A. FOWLEY, D. MICHOS, X.-L. LUO and R. H. CRABTREE, *Tetrahedron Lett.*, 1993, 34, (19), 3075–3078

Colloidal Pd formed in organic solvents from Pd(hfacac)₂, where hfacac = CF₃COCHCOF₃, and silane or a Si-H-containing polymer, such as polymethylhydrosiloxane, is an active, stable and selective catalyst for hydrogenation and dehydrohalogenation. Under H₂ the hydrogenation rates were fast, indicated by Pd precipitation, after only minutes at 25°C. The system is highly selective and other known Pd(0) catalysed reactions, such as reductive amination and hydroboration of olefins, etc., did not occur.

Water Facilitation of Palladium-Mediated Coupling Reactions

H.-C. ZHANG and G. D. DAVES, *Organometallics*, 1993, 12, (5), 1499–1500

In H₂O containing media, Pd-catalysed coupling reactions, which do not take place using organic media, were readily achieved. For Pd mediated coupling reactions of iodo derivatives of N heterocycles with cyclic enol ethers and furanoid glycols, using Pd(OAc)₂ catalyst, H₂O containing solvent systems are more effective than organic systems.

Hydroformylation of 2,3- and 2,5-Dehydrofurans in the Presence of a Homogeneous Catalytic Complex on the Basis of AcAcRh(CO)₂ Modified with Various Phosphites

A. L. LAPIDUS, I. G. PRUIDZE, G. A. KORNEEVA, M. M. VARTANYAN, A. P. ROBIN, E. V. SLIVINSKII, A. V. DOLIDZE and S. M. LOKTEV, *Neftekhimiya*, 1993, 33, (2), 102–113

Rh catalysts based on AcAcRh(CO)₂ + 9L where L = phenyl-3,3,5,5-tetra-tert-butyl-1,1-biphenyl-2,2-diylphosphite (organophosphite) or etriol phosphite, were studied during hydroformylation of 2,3- and 2,5-dehydrofurans (DHF). Hydroformylation of 2,3-DHF was regioselective to 2-formyltetrahydrofuran in the presence of organophosphite and to 3-formyltetrahydrofuran with etriol phosphite.

Rhodium-Mediated 100% Regioselective Oxidative Hydroamination of α -Olefins

J.-J. BRUNET, D. NEIBECKER and K. PHILIPPOT, *Tetrahedron Lett.*, 1993, 34, (24), 3877–3880

The system generated from LiNHPh and [(Et₃P)₂RhCl]₂ catalyses the regioselective condensation of aniline with styrene to give mixtures of PhNH-CH(CH₃)Ph and PhN=C(CH₃)Ph, which are hydroamination and oxidative hydroamination products, respectively, in ~ 1 : 2 ratio. The overall reaction was slow, but no deactivation was observed for 12 days (turnover 21). This 100% regioselective oxidative hydroamination was confirmed for 1-hexene.

Poly(trimethylolpropane)trimethacrylate-Bound Rh-Phosphine Complexes as Catalysts in Continuous Gas-Phase Hydroformylation of Propene

B. HEINRICH, J. HJORTKJAER, A. NIKITIDIS and C. ANDERSSON, *J. Mol. Catal.*, 1993, 81, (3), 333–347

Studies of poly-TRIM-bound Rh catalysts prepared by reactions of the title polymer supports and a grafted linear acrylate polymer bearing phosphines, with [Rh(acac)(CO)₂] were performed during a continuous gas-phase hydroformylation of propene. At 333 K and P_{tot} 600 kPa, the catalysts were active and stable.

Uniform Colloids of Ruthenium Dioxide Hydrate Evolved by the Surface-Catalyzed Reduction of Ruthenium Tetroxide

H. N. McMURRAY, *J. Phys. Chem.*, 1993, 97, (30), 8039–8045

Electrostatically stabilised submicron colloids of RuO₂·xH₂O were prepared by the reduction of near neutral aqueous solutions of RuO₄. After nucleation, colloidal particles grew spontaneously by heterogeneously catalysing the reduction of RuO₄ by H₂O. A mechanism is proposed whereby the growing particles act as microelectrodes which couple the reversible cathodic reduction of RuO₄ and the irreversible anodic oxidation of H₂O.

FUEL CELLS

Effect of Sputtered Film of Platinum on Low Platinum Loading Electrodes on Electrode Kinetics of Oxygen Reduction in Proton Exchange Membrane Fuel Cells

S. MUKERJEE, S. SRINIVASAN and A. J. APPLEBY, *Electrochim. Acta*, 1993, 38, (12), 1661–1669

Localisation of Pt electrocatalyst by sputter deposition of a thin film (500 Å) on the front surface of a fuel cell electrode containing a supported electrocatalyst, 20% Pt/C at 0.4 mg/cm² loading, exhibits higher fuel cell performance than an electrode without the sputtered film. Comparison of cell performance at 5 atm and 95°C showed a 4-fold increase in the O reduction reaction at 0.9 V vs. RHE and a similar 3.6-fold increase in the exchange current densities.

Development and Evaluation of Platinum-Ruthenium Bimetal Catalyst-Based Carbon Electrodes for Hydrogen/Oxygen Fuel Cells in NaOH Media

S. M. A. SHIBLI and M. NOEL, *J. Power Sources*, 1993, 45, (2), 139–152

Teflon bonded, Pt-Ru catalyst based, porous-C gas-diffusion electrodes, were fabricated for alkaline H₂/O₂ fuel cells. The parameters of fabrication, such as hot-pressing temperature, compaction load, duration of hot pressing and binder composition, were optimised to be 623 K, 150 kg/cm², 120 s and 20 wt.%, respectively. Optimum composition was 2.5 wt.% Pt-5 wt.% Ru giving current density of 150 mA/cm² at 0.65 V.

A Novel Pd-Ag Membrane Anode for Alkaline Fuel Cells Suitable for CO₂-Containing Hydrogen

P. HASLER and T. ALLMENDINGER, *J. Power Sources*, 1993, 45, (1), 93-103

A novel type of a selective H permeable Pd membrane, consisting of a poreless Pd-Ag film 1 μm in thickness on a Ni-sieve structure support, is presented. A palladated and additionally platinated membrane was tested as a H anode in 10 M KOH at 55-106°C. At an overpotential of 100 mV and at 120°C, a current density ~ 0.5 A/cm² was estimated for pure H and normal pressure.

High Power Density Solid Oxide Electrolyte Fuel Cells Using Ru/Y₂O₃ Stabilized Zirconia Cermet Anodes

M. SUZUKI, H. SASAKI, S. OTOSHI, A. KAJIMURA and M. IPPOMATSU, *Solid State Ionics*, 1993, 62, (1,2), 125-130

High performance Ru/YSZ cermet solid oxide electrolyte fuel cell (SOFC) anodes were fabricated by the CVD-EVD method. During the power generation tests at 1273 K, the Ru/YSZ cermet anode showed higher activity for H oxidation compared to conventional Ni/YSZ cermet anodes. At current density of ≤ 3200 mA/cm², the AC polarisation value was reduced to ~ 200 mV. The cells had the highest power generation density of 1550 mW/cm².

ELECTRICAL AND ELECTRONIC ENGINEERING

Surface Effects on Leakage Current and Lifetime in Pt Diffused Planar Silicon p⁺n Diodes

P. SAGALA, C. SHU and H. KUWANO, *Jpn. J. Appl. Phys., Part 1*, 1993, 32, (5A), 1875-1878

Studies of the effect of Pt diffusion on leakage current and lifetime in conventional planar Si p⁺n diodes with metal oxide semiconductor structure were performed during 40 min diffusion of Pt into gate-controlled Si p⁺n diodes at 800-1000°C. The surface covered with oxidised Si had a significant effect on the leakage current, but no effect on the lifetime.

Magnetic Properties and Read/Write Characteristics of Co-Cr-(Pt,Ta)/(Cr-Ti,Cr) Thin Film Media

Y. SHIROISHI, Y. HOSOE, A. ISHIKAWA, Y. YAHISA, Y. SUGITA, H. SUZUKI, T. OHNO and M. OHURA, *J. Appl. Phys.*, 1993, 73, (10), 5569-5571

A Cr-Ti underlayer enhances the in-plane coercive forces of Co-Cr-Pt and Co-Cr-Ta films giving a maximum coercive force of 3.5 kOe for (CoCr_{0.15})_{0.84}Pt_{0.10}/CrTi_{0.2}. The C/Co-Cr-Pt/Cr-Ti thin film media with high coercive forces show excellent read/write characteristics. The linear densities at 50% signal drop are very high, 175 and 101 kFCI, for the C/Co-Cr-Pt/Cr-Ti media at head-to-magnetic layer spacings of 0.01 and 0.07 μm.

Influence of Contact Surface Conditions on Discharge Phenomena of Vacuum Reed Switches

K. HINOHARA, T. KOBAYASHI and C. KASAKITA, *IEEE Trans. Components, Hybrids, Manuf. Technol.*, 1993, 16, (2), 170-173

The effects of surface deactivation treatment on breakdown voltage, amount of O and work function were examined for three types of vacuum reed switches. One sample was Rh plated with no treatment, the other two samples were Rh plated with surface deactivation by O treatment at 450 and 475°C. The Rh₂O₃ film produced through the O treatment enhanced the work function of the contact surface and this in turn increased breakdown voltage between contacts. The thickness of the Rh oxide film is considered to increase as the treatment temperature rises.

Thermal Stability of Rapidly Annealed Ruthenium n-GaAs Schottky Contacts

G. EFTEKHARI, *Jpn. J. Appl. Phys., Part 1*, 1993, 32, (5A), 1934-1935

Studies of the thermal stability of Ru n-GaAs contacts annealed for 15 s at 200-800°C showed that the contacts annealed at ≤ 750°C were stable. However at > 750°C, a sharp decrease in barrier height was observed while the ideality factor and reverse current showed a sharp increase. This may be due to chemical reactions occurring at the interface at higher temperatures (~ 750°C) compared with the furnace annealing temperature (~ 450°C).

Josephson Coupling of YBa₂Cu₃O_{7-x} through a Ferromagnetic Barrier SrRuO₃

L. ANTOGNAZZA, K. CHAR, T. H. GEBALLE, L. L. H. KING and A. W. SLEIGHT, *Appl. Phys. Lett.*, 1993, 63, (7), 1005-1007

The electrical properties of superconductor-normal-superconductor Josephson junctions based on YBCO with SrRuO₃ barrier layers is reported. At small barrier thicknesses the SrRuO₃ junctions followed the behaviour of non-ferromagnetic but closely related CaRuO₃ junctions. A rapid disappearance of critical current was observed when the barrier thickness was increased to 250 Å.

MEDICAL USES

Monoamineplatinum(II) Complexes Conjugated to Water-Soluble Carrier Polymers for Chemotherapeutic Applications

C. W. N. MBONYANA, E. W. NEUSE and A. G. PERLWITZ, *Appl. Organomet. Chem.*, 1993, 7, (4), 279-288

The synthesis of conjugate complexes of a Pt complex and a polymer carrier with carcinostatic activity, where each Pt atom is co-ordinated to a single primary amine ligand of the H₂O soluble polyaspartamide carrier is described. The carriers are platinated by treatment with K₂PtCl₆ at 25-60°C in pH range 5-6, and the polymer-Pt conjugates are purified by aqueous phase dialysis and freeze-drying.