

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

An XPS Study of Nitric Oxide, Carbon Monoxide and Oxygen Adsorption on Pt(210)

J. F. LANG and R. I. MASEL, *Surf. Sci.*, 1986, **167**, (2/3), 261-270

XPS and AES were used to examine the adsorption of NO, CO and O₂ on Pt(210). Both CO and NO adsorb molecularly on Pt(210), but while CO desorbs without dissociation, NO dissociates on heating to 450K. O₂ adsorbs dissociatively. Two different O states are seen by XPS, and the Pt(210) surface seems to adsorb an unusually large amount of O₂.

The Al-Pt (Aluminum-Platinum) System

A. J. McALISTER and D. J. KAHAN, *Bull. Alloy Phase Diagrams*, 1986, **7**, (1), 47-51, 83-84

The Al-Pt phase diagram is discussed. The phase in equilibrium with Al, and the liquid near 20at.%Pt at 657°C are contentious, as is the existence of the high- and low-temperature modification of AlPt₃. Other problems are examined, and data on crystal structures and lattice parameters are given.

The Glass Transition Phases in the Formation of Pt-Si

D. M. VANDERWALKER, *Phys. Status Solidi A*, 1986, **94**, (1), 77-81

A crystalline to amorphous transition occurs at the Pt-Si interface during the formation of PtSi. The structure of the glassy phase depends on temperature. At higher temperatures the glassy phase contains small randomly oriented Pt crystals; while the lower temperature glass has a continuous amorphous structure. When Pt diffuses into Si a crystalline-amorphous transition occurs, when the elastic energy of the crystalline solid is increased and the energy barrier for the reaction is lowered. PtSi nucleates within the glass at one interface.

Metallic Conduction through Langmuir-Blodgett Films

N. R. COUCH, C. M. MONTGOMERY and R. JONES, *Thin Solid Films*, 1986, **135**, (2), 173-182

The mechanism giving rise to high electrical conductivity was examined in Au-Pd/Cd stearate/Au and Ag/ ω -tricosenoic acid/Ag systems, where the Cd stearate and ω -tricosenoic acid are Langmuir-Blodgett films. Metallic pathways, of area $6 \times 10^{-3} \mu\text{m}^2$, exist through the LB films, even for relatively thick multilayers ($N \approx 40$ layers). Switching effects were observed in these filaments on the application of voltage pulses.

Phase Relationships in the Ternary System U-Nd-Pd

D. G. PARNELL, N. H. BRETT, H. R. HAINES and P. E. POTTER, *J. Less-Common Met.*, 1986, **118**, (1), 141-152

Phase equilibria in the U-Nd-Pd system have been obtained by a variety of techniques. Also information on the binary phase diagrams for U-Nd, U-Pd and Nd-Pd is reviewed. Data obtained from quenched and annealed samples show that a liquid immiscibility gap exists within the system. Solid state tie lines have been determined.

Hydrogen Chemisorption on, and Diffusion through, Palladium Clusters

N. A. BAYKARA, J. ANDZELM, D. R. SALAHUB and S. Z. BAYKARA, *Int. J. Quantum Chem.*, 1986, **29**, (4), 1025-1032

Computations were performed for PdH, Pd₃H and for a series of Pd₁₀H clusters representing H chemisorbed on a (111) surface and at various sites along a diffusion path through the cluster. The calculated chemisorption geometry has a Pd-H distance of 1.72Å.

CHEMICAL COMPOUNDS

Redox Properties of the Oxo-Bridged Osmium Dimer[(bpy)₂(OH₂)Os^{III}OOs^{IV}(OH)(bpy)₂]⁴⁺. Implications for the Oxidation of H₂O to O₂

J. A. GILBERT, D. GESELOWITZ and T. J. MEYER, *J. Am. Chem. Soc.*, 1986, **108**, (7), 1493-1501

The oxo-bridged Os dimer title compound has been isolated and characterised. Electrochemical experiments have revealed an extensive redox chemistry for the dimer based couples, for example Os(V)Os(V)/Os(IV)Os(V).

The Next Generation of (Polyazine)-Ruthenium(II) Complexes

K. J. BREWER, W. R. MURPHY, S. R. SPURLIN and J. D. PETERSEN, *Inorg. Chem.*, 1986, **25**, (6), 882-884

The synthesis and characterisation of a new and highly luminescent Ru complex, Ru(dpp)₃²⁺ (dpp) = 2,3-bis(2-pyridyl)pyrazine, is reported. The Ru(dpp)₃²⁺ excited state lifetime is shorter than that of the bpy analogue, but the former complex has a greater advantage in energy storage and transfer reactions. Dpp can bind as a chelate to a second metal centre, enabling the Ru(dpp)₃²⁺ complex to be the centre for formation of complexes capable of intramolecular energy- or electron-transfer reactions.

Synthesis and Sintering of Mixed Metallic Oxide Conductors $\text{Nd}_{2-x}\text{Cu}_x\text{Ru}_2\text{O}_{7-x}$

A. HAOUZI, J. MULLER and J. C. JOUBERT, *J. Phys. (Paris), Colloq. 1*, 1986, C1-855-C1-859

Pyrochlore type phases $\text{Nd}_{2-x}\text{Cu}_x\text{Ru}_2\text{O}_{7-x}$ were synthesised up to $x=0.375$. Samples with good compactness have good metallic conductivity, but those with bad compactness behave as semiconductors. Good sintering has been obtained with the addition of 5wt.%CuO. Samples sintered with CuO are then metallic, for all values of x except 0.

ELECTROCHEMISTRY

Electrochemical Behavior and Surface Structure of Pt Thin Film Electrodes Deposited on Molecularly Smooth Mica

M. MAEDA, H. S. WHITE and D. J. McCLURE, *J. Electroanal. Chem. Interfacial Electrochem.*, 1986, 200, (1 and 2), 383-387

A preliminary note on results of the preparation and characterisation of 10nm thick semitransparent Pt film electrodes with an average surface roughness of 1nm is presented. The electrochemical behaviour of the electrodes was qualitatively similar to that of macroscopic polycrystalline Pt electrodes. The Pt/mica structures are well suited for electrochemical studies and in thin-film technology.

Effect of Electrochemical Pretreatment on Catalytic Activity of Bismuth Ruthenate Electrodes for Oxygen Evolution in Alkaline Solution

C. IWAKURA, T. EDAMOTO and H. TAMURA, *Bull. Chem. Soc. Jpn.*, 1986, 59, (2), 145-148

The catalytic activity of a film-type Pt/Bi₂Ru₂O₇ electrode for O₂ evolution was greatly enhanced by an electrochemical pretreatment, including potential holding and cycling. However no appreciable enhancement in catalytic activity was observed for a pellet-type Bi₂Ru₂O₇. The pretreatment effect was explained by the participation of higher valence Ru species in the O evolution reaction.

Polarization Behavior and Components of Internal Resistances of Semi-Polar Type Pt-SPE (Nafion 315) Electrodes

K. FUJIKAWA, H. ISHIKAWA, H. NAKAJIMA and H. KITA, *Denki Kagaku*, 1986, 54, (1), 55-59

The electrochemical behaviour of a Pt-SPE (Nafion 325) electrode was investigated for H ionisation and O reduction reactions by polarisation. The O reduction and the H ionisation are examined as polarisation curves by reference to Tafel slopes, Ohm's law and the limiting current, depending upon the potential, gas pressure and type of reaction. It is concluded that a semimicro model of the Pt-SPE electrode is applicable when the catalytically active zone is just inside the membrane surface, embedding Pt.

An X-Ray Photoelectron Spectroscopic Study of Electrocatalytic Activity for Chlorine Evolution on Amorphous Palladium-Phosphorus Alloys Containing Rhodium, Iridium or Platinum

M. HARA, K. ASAMI, K. HASHIMOTO and T. MASUMOTO, *Electrochim. Acta*, 1986, 31, (4), 481-488

The electrocatalytic activity for Cl₂ evolution was examined in terms of the surface film formed on amorphous Pd-base alloy anodes during hot concentrated NaCl electrolysis. Cl₂ occurred on the surface film where cations were Rh, Ir or Pt. Amorphous Pd-Ir-P alloys had high activity for Cl₂ evolution, while Pd-Rh-P and Pd-Pt-P alloys needed high overpotential for Cl₂ evolution. A large amount of Cl₂ was found on the surface of amorphous Pd-Rh-P and Pd-Pt-P alloys polarised at high overpotentials.

Indirect Electrooxidation of Alcohols and Aldehydes by Using a Double Mediator System Consisting of RuO₄/RuO₂ and Cl⁺/Cl⁻ Redoxes in an Aqueous-Organic Two-Phase System

S. TORII, T. INOKUCHI and T. SUGIURA, *J. Org. Chem.*, 1986, 51, (2), 155-161

The utility of a double mediator system consisting of RuO₄/RuO₂ and Cl⁺/Cl⁻ redox couples for the indirect electrooxidation of alcohols and aldehydes has been examined. RuO₄ oxidised the substrate, then RuO₄ was regenerated from RuO₂ by Cl₂ or [Cl]⁺, and the Cl ion was oxidised to [Cl]⁺ on the anode in the aqueous layer. The simplicity of product isolation and low cost of the oxidants make this an alternative to standard methods of oxidation. Secondary alcohols were oxidised to ketones, and primary alcohols and aldehydes were oxidised to carboxylic acids.

PHOTOCONVERSION

Photochemical Hydrogen Production with Platinized Suspensions of Cadmium Sulfide and Cadmium Zinc Sulfide Modified by Silver Sulfide

J.-F. REBER and M. RUSEK, *J. Phys. Chem.*, 1986, 90, (5), 824-834

Active photocatalysts for the photochemical production of H₂ can be prepared by Pt deposition on microcrystals of pure CdS powders with very small (<6.7m²/g) specific surface areas. The H₂ evolution comes from irradiating suspensions of platinised CdS in solutions of S²⁻ and/or SO₃²⁻ ions. Also Ag₂S coprecipitated with CdS or surface modification of CdS with large (>>100m²/g) specific area by Ag⁺ ions allowed very active platinised photocatalysts to be prepared for H₂ photochemical production from solutions containing S²⁻ ions. Sulphite ion addition allows H₂ to be evolved at a higher rate. The platinised pure CdS powder with low specific areas are the most stable photocatalysts.

Polymer Viologen as a Stabilizing Agent of Colloidal Platinum for Photoinduced Electron Transfer Reactions

Y. NOSAKA, A. KUWABARA and H. MIYAMA, *J. Photochem.*, 1986, **32**, (2), 143-150

Photoinduced electron transfer and H evolution were investigated using colloidal Pt stabilised by viologen-pendant Nylon (Pt-PV²⁺). From laser flash photolysis experiments the Pt-PV²⁺ was found to accept directly an electron from excited ZnTMPyP⁴⁺, and the reverse electron transfer was retarded by the positive charge of the protecting polymer, while no net electron transfer was observed for colloidal Pt stabilised by PVA. The quantum yield of H production with a Pt-PV²⁺ catalyst was a factor of 7 higher than with Pt-PVA, and reached 0.38.

Colloidal Platinum Protected by Polymerized Micelle. Preparation and Application to Catalysis for Photochemical Hydrogen Generation from Water

N. TOSHIMA, T. TAKAHASHI and H. HIRAI, *Chem. Lett. Jpn.*, 1986, (1), 35-38

Colloidal Pt protected by polymerised micelles was prepared by the photoreduction of chloroplatinic acid in the presence of unsaturated surfactants, and the subsequent u.v.-polymerisation of the surfactants. This colloidal Pt acts as an active catalyst in the EDTA/Ru(bpy)₃²⁺/MV²⁺ system.

Photoresponsive Graphite Electrode Coated with Bilayer Membranes of Prussian Blue and Polymer-Pendant Ru(bpy)₃²⁺

M. KANEKO and A. YAMADA, *Electrochim. Acta*, 1986, **31**, (2), 273-275

Graphite electrodes were made photoresponsive by coating with bilayer membranes of Prussian blue and polymer-pendant Ru(bpy)₃²⁺. A photocurrent was induced by irradiating the coated electrode, which was dipped in aqueous electrolyte. Photocurrent depends on the applied potential, and the major process for photocurrent generation concerns the excitation of the Ru complex.

Photodynamics of the Tris (2,2'-bipyrazine)Ruthenium(2+)/Methylviologen/EDTA System in Aqueous Solution

D. R. PRASAD and M. Z. HOFFMAN, *J. Am. Chem. Soc.*, 1986, **108**, (10), 2568-2573

Luminescence quenching and flash photolysis have been used to study the photodynamics of the title system in aqueous solution. The quantum yields were found in acid, neutral and alkaline solutions. Ru(bpz)₃²⁺ is concluded to be a superior photosensitiser than Ru(bpy)₃²⁺ because its excited state favours reductive quenching by sacrificial electron donors, the oxidised forms of which can undergo rapid irreversible transformation.

Photodecomposition of H₂S in Aqueous Alkaline Media Catalyzed by RuO₂-Loaded Alumina in the Presence of Cadmium Sulfide. Application of the Inter-Particle Electron Transfer Mechanism

E. BORGARELLO, N. SERPONE, M. GRÄTZEL and E. PELIZZETTI, *Inorg. Chim. Acta*, 1986, **112**, (2), 197-201

The photodecomposition of H₂S by visible light >400nm has been investigated in 0.1M Na₂S and 1MNaOH in the presence of CdS dispersions and in CdS + Al₂O₃/RuO₂ mixtures. A 5-fold increase in the H₂ evolution rate is obtained through the coupling of the excited semiconductor and the redox catalyst. Data are interpreted by the inter-particle electron transfer pathway. The engineering energy efficiency is estimated at 1.2% from the total incident light energy and the heat of combustion of H₂.

Photogeneration of Hydrogen and Sulfur on Polypyrrole/RuO₂ Modified Silicon Powder

B. C. CHUN YU, S. KAPUSTA and N. HACKERMAN, *J. Electrochem. Soc.*, 1986, **133**, (5), 934-935

The illumination of polypyrrole/RuO₂ loaded Si particles dispersed in aqueous sulphide solutions results in the generation of large amounts of H₂ and colloidal S (or polysulphides). The S is removed with a current efficiency >90% and quantum efficiency of ~1%.

Surface Structure and Properties of Zeolite-Supported Transition Metal Oxide Catalysts for Photooxidation of Water to Oxygen

M.-X. YANG, C.-L. LI, Y.-M. ZHANG and C.-L. GU, *J. Catal. (Dalian, China)*, 1986, **7**, (1), 60-66

Surface structure and properties of RuO_x/Y and FeO_x/Y zeolite catalysts were studied by various techniques. RuO_x/Y + FeO_x/Y(1) contains many more acid sites than the corresponding co-impregnated catalyst (RuO_x-FeO_x)/Y(2). (1) and (2) have quite different properties, composition and morphological structure.

ELECTRODEPOSITION AND SURFACE COATINGS

Electroless Plating for Electronics

W. J. HAWK, *Metal Finish.*, 1986, **84**, (3), 11-12

Properties of electroless Pd, operating characteristics, solderability and contact resistance are discussed. Electroless plating without a Au overlayer is cost effective and provides equivalent or improved performance over previously used Au finishes. Wear cycle life increases from 100,000 for 50 microinches of Au to >10⁶ for 50 microinches of Pd. A dual tank system is recommended and 50 microinches is proposed to provide the desired properties.

Gold Flashed Palladium Nickel for Electronic Contacts

K. J. WHITLAW, *Trans. Inst. Met. Finish.*, 1986, **64**, (2), 62-67

The results of comparisons between Pd-Ni and acid hard Au in high speed plating applications shows that similar plating rates can be achieved by using a new high speed Pd-Ni process. Tables of mechanical endurance and industrial atmosphere tests, and current switching valves are given for Pd-Ni/Cu, Pd-Ni/Ni, Au flash/Pd-Ni/Cu and Au flash/Pd-Ni/Ni. The Pd-Ni electrolyte produces a deposition rate of 18 μ m/min during high speed plating. It was found that Au flashed Pd-Ni is a suitable alternative to acid hard Au.

LABORATORY APPARATUS AND TECHNIQUE

Platinum Black Powder as a Heat Exchanger Material at Low Temperatures

P. R. ROACH, Y. TAKANO, R. O. HILLEKE, M. L. VRTIS, D. JIN and B. K. SARMA, *Cryogenics*, 1986, **26**, (5), 319-321

A procedure for producing a thin layer of sintered Pt powder with a very large surface area, relatively low electrical resistivity and a reasonably small void volume has been developed for use in cooling He to low temperatures.

A Proton-Injecting Technique for the Measurement of Hydration-Dependent Protonic Conductivity

H. MORGAN, R. PETHIG and G. T. STEVENS, *J. Phys. E*, 1986, **19**, (1), 80-82

A technique for injecting protons directly from a H-saturated Pd black electrode into a solid sample is described. This technique could be used for measurements on H bonded solids, crystalline ionic hydroxides and acids, ceramics and biopolymers. Pd black electrodes can reversibly absorb H to 900 volumes of H₂ at NPT. In the Pd lattice the dissolved H is almost completely ionised. The conductivity cell where the sample under test is between two Pd black electrodes is described.

HETEROGENEOUS CATALYSIS

Kinetics and Reaction Pathways of Methanol Oxidation on Platinum

R. W. McCABE and D. F. MCCREADY, *J. Phys. Chem.*, 1986, **90**, (7), 1428-1435

Methanol oxidation rates on Pt wires in a flow reactor at pressures 30-130Pa were studied as functions of oxygen-to-methanol equivalence ratio and wire temperature. Methanol oxidation followed two paths, a major pathway involving H₂CO and CO intermediates and a minor pathway involving an elemental C intermediate.

Cyclic Operation of Pt/Al₂O₃ Catalysts for CO Oxidation

B. K. CHO and L. A. WEST, *Ind. Eng. Chem., Fundam.*, 1986, **25**, (1), 158-164

An examination of CO oxidation over well-characterised Pt/Al₂O₃ catalysts in an integral reactor under forced feed composition cycling is presented to determine improvements in the cyclic performance of automotive catalysts. The most effective CO oxidation strategy is a hybrid scheme based on cyclic operation during the warm-up period to 300°C, then steady state operation at temperatures >300°C.

Selective Conversion of Propane into Aromatics on Platinum Ion-Exchanged Gallium-Silicate Bifunctional Catalysts

T. INUI, Y. MAKINO, F. OKAZUMI and A. MIYAMOTO, *J. Chem. Soc., Chem. Commun.*, 1986, (7), 571-573

Novel Pt ion-exchanged Ga silicate bifunctional catalysts have been developed. The catalysts produced aromatics from propane more actively and selectively than previously developed catalysts.

Oxygen Storage in Automobile Exhaust Catalyst

I. S. METCALFE and S. SUNDARESAN, *Chem. Eng. Sci.*, 1986, **41**, (4), 1109-1115

Charge transfer reactions between a Pt catalyst and Y-stabilised zirconia support were studied electrochemically during CO oxidation over a range of compositions and temperatures typical of automotive exhausts. A model for the participation of the support in the oxidation reactions is derived. It is estimated that the contribution of the charge transfer reactions occurring at the three-phase interface between Pt, YSZ and the gas phase, to the total area of CO oxidation is negligible under steady conditions.

Platinum-Rhodium Synergism in Three-Way Automotive Catalysts

S. H. OH and J. E. CARPENTER, *J. Catal.*, 1986, **98**, (1), 178-190

The interactions between Pt and Rh in three-way automotive catalysts were investigated with a Pt-Rh bimetallic catalyst and a mixture of Pt and Rh monometallic catalysts, while keeping the amount of each noble metal constant. CO oxidation for the bimetallic catalyst was substantially higher than for the mixture, over converter warm-up conditions.

Method for the Selective Hydrogenation of Polyunsaturated Hydrocarbons in Olefinic Hydrocarbon Mixtures

F. NIERLICH and F. OBENAU, *Erdoel Kohle Erdgas Petrochem.*, 1986, **39**, (2), 73-78

The qualitative and selective hydrogenation of polyunsaturated hydrocarbons, such as dienes or acetylenes, in olefinic hydrocarbon mixtures, to the corresponding monoolefins occurs over a Pd/Al₂O₃ or Pd/C catalyst in the presence of a few ppm of CO.

NO Reduction Activity of Pd Catalyst Modified with Rare Earth Oxides

H. MURAKI, M. FUKUI, K. YOKOTA and Y. FUJITANI, *Nippon Kagaku Kaishi*, 1986, (2), 130-137

The reduction of NO on fresh and aged Pd-rare earth/ α -Al₂O₃ catalyst was investigated using simulated exhaust gas as NO. NO conversion at lower temperatures was better with Pd-rare earth catalysts than with unmodified Pd. La, Nd and Sm were the most effective additions to Pd. Except for Pd-Ce the Pd-rare earth catalysts had better activities and selectivities below 300°C for the NO-H₂ reaction than Pd.

Studies of the Interactions of H₂ and CO with Pd/SiO₂ Promoted with La₂O₃, CeO₂, Pr₆O₁₁, Nd₂O₃ and Sm₂O₃

J. S. RIECK and A. T. BELL, *J. Catal.*, 1986, 99, (2), 278-292

The interactions of H₂ and CO with promoted Pd/SiO₂ were investigated by various techniques. The promoter partially covers the Pd particles, and on reduction parts of the promoter in contact with Pd are reduced. The partially reduced rare earth oxide species covering the Pd reduces the amounts of H₂ and CO that can be adsorbed on the metal. The rare earth oxide moieties have a slight influence on H₂ adsorbed distribution but cause a significant change in the distribution of CO adstates.

Soybean Oil Hydrocracking under Pressure: Process and General Aspect of the Transformation

P. P. NUNES, D. BRODZKI, G. BUGLI and G. D. JEGAMARIADASSOV, *Rev. Inst. Fr. Pet.*, 1986, 41, (3), 421-432

A process for studying the hydrocracking of vegetable oils into gasoline and diesel fuel fractions while limiting polymerisation and coking is proposed. The hydrocracking utilised an oxide or a dual-function 2%rhodium/silica catalyst. During the hydrogenating/cracking with 2%Rh/SiO₂, the double bonds of the lateral chains of triglycerides were hydrogenated on heating to ~673K, when hydrocracking began. At 673K the decarbonylation/decarboxylation of fatty acids is observed.

Trifunctional Catalysts for Conversion of Syngas to Alcohols. Fifth Quarterly Report, September 1-November 30, 1985

K. B. BISCHOFF, W. MANOGUE and G. A. MILLS, *NTIS Chemistry*, 15 April 1986, 86, (15), 8-9

The individual reaction products formed during CO hydrogenation over Rh catalysts have been identified and contain significant amounts of alcohols, aldehydes, acids, esters, ethers, C₁ to C₅ hydrocarbons, CO₂ and H₂O. Na-Rh/Al₂O₃ catalyst was used in CO hydrogenation; the selectivity to oxygenates decreased with increasing conversion, and C₂ oxygenates were ~80% of all oxygenates formed.

Hydrogenation of CO and CO₂ on Carbon Black-Supported Ru Catalysts

I. RODRÍGUEZ-RAMOS, F. RODRÍGUEZ-REINOSO, A. GUERRERO-RUIZ and J. DE DIOS LÓPEZ-GONZÁLEZ, *J. Chem. Technol. Biotechnol.*, 1986, 36, (2), 67-73

The activity and selectivity of unsupported Ru and Ru/C black catalysts for the hydrogenation of CO and CO₂ has been examined in terms of particle size effects. The specific activities for both reactions decreased with metal particle size, and the product distribution for CO hydrogenation was also a function of metal dispersion. CO₂ hydrogenation yields only CH₄. Thus the proportion of CH₄ produced increases and the olefin:paraffin ratio decreases with decreasing Ru particle size.

HOMOGENEOUS CATALYSIS

Reactions of Rh(acac)[P(OPh)₃]₂ with H₂, CO and Olefins

A. M. TRZECIAK, J. J. ZIOLKOWSKI, S. AYGEN and R. VAN ELDIK, *J. Mol. Catal.*, 1986, 34, (3), 337-343

The reactions of the title compounds have been studied by various techniques. In the presence of H₂ and free phosphite, Rh(acac)P₃ produces HRhP₄, which catalyses the isomerisation of olefins. Adding CO to HRhP₃ produced HRh(CO)P₃, which was a good hydroformylation catalyst. The latter hydride can be directly obtained from the starting complex in the presence of H₂, CO and free phosphite.

Catalytic Reactions of Metalloporphyrins. I. Catalytic Modification of Borane Reduction of Ketone with Rhodium(III) Porphyrin as Catalyst

Y. AOYAMA, T. FUJISAWA, T. WATANABE, H. TOI and H. OGOSHI, *J. Am. Chem. Soc.*, 1986, 108, (5), 943-947

A highly efficient catalytic modification of synthetic reactions of borane in the presence of O₂ is provided by a Rh porphyrin catalyst. The Rh-BH₄ complex can transfer borane to ketone, do a facile oxidation with O₂ and easy hydrolysis with H₂O.

Chemistry and Catalytic Properties of Ruthenium and Osmium Complexes. 3. Development of Highly Active Systems for the Homogeneous Hydrogenation of Aldehydes and Ketones

R. A. SÁNCHEZ-DELGADO, N. VALENCIA, R.-L. MÁRQUEZ-SILVA, A. ANDRIOLLO and M. MEDINA, *Inorg. Chem.*, 1986, 25, (8), 1106-1111

The development of highly efficient catalytic systems from 19 Ru and 4 Os complexes containing hydride, phosphine and carboxylate ligands under moderate reaction conditions is described for the catalytic hydrogenation of aldehydes and ketones to yield the corresponding alcohols. For complexes MHX(CO)(PR₃)₂, the catalytic activity is dependent on X (halide), but independent of R.

Homogeneous Multimetallic Catalysts. Part 6. Hydroformylation and Hydroesterification of Olefins by Homogeneous Cobalt-Ruthenium Bimetallic Catalysts

M. HIDAI, H. FUKUOKA, Y. KOYASU and Y. UCHIDA, *J. Mol. Catal.*, 1986, **35**, (1), 29-37

The $\text{Co}_2(\text{CO})_8$ - $\text{Ru}_3(\text{CO})_{12}$ system showed high catalytic activity for hydroformylation of olefins such as cyclohexene, 1-hexene and styrene compared to the catalysts singly. The hydroformylation reaction was much influenced by the solvent used, and methanol and ethanol were the best of those employed.

Oxidation of Alcohols with Allyl Methyl Carbonate by Means of Ruthenium Catalyst

I. MINAMI, M. YAMADA and J. TSUJI, *Tetrahedron Lett.*, 1986, **27**, (16), 1805-1808

Oxidation reactions for alcohols were attempted with various Pd, Rh and Ru catalysts. It was found that for secondary and allylic alcohols 1mol.% of Ru catalysed reactions with allyl methyl carbonate giving ketones or α,β -unsaturated aldehydes.

FUEL CELLS

Electrocatalysis by Electrodeposited Pt from PtCl_2^- Confined in a Langmuir-Blodgett Film on a Glassy Carbon Electrode

M. FUJIHARA and S. POOSITTISAK, *J. Electroanal. Chem. Interfacial Electrochem.*, 1986, **199**, (2), 481-484

A novel Pt modified GC electrode with a much lower loading level and similar activity to smooth Pt has been developed using the Langmuir-Blodgett technique. The overlay is so thin (~10nm) that the high catalytic activity cannot be limited by mass transfer through the film. The electrodes are designed for fuel cells. Cyclic voltammograms are presented.

CHEMICAL TECHNOLOGY

Application of Platinum Gauze Activated by Hydrogen to the Adsorption Separation of Silver Traces and Their Determination by AAS or Spectrophotometry

Z. BOGUSZEWSKA, M. KRASIEJKO and B. PALMOWSKA-KUŚ, *Talanta*, 1986, **33**, (2), 155-160

The separation of Ag from Cu by deposition through internal electrolysis with H adsorbed on a Pt gauze electrode surface is described. The H adsorbed on the Pt gauze lowers the electrode potential, allowing Ag traces to be deposited. The Pt surface activation by H can be achieved either electrolytically or by passing H₂ through the solution in which the Pt is immersed. Ag can then be stripped from the gauze electrode. This method can also be used for purification of reagents containing Ag traces.

ELECTRICAL AND ELECTRONIC ENGINEERING

High Output Power Hydrogen Engine with High Pressure Fuel Injection, Hot Surface Ignition and Turbocharging

S. FURUHAMA and T. FUKUMA, *Int. J. Hydrogen Energy*, 1986, **11**, (6), 399-407

A high power two-stroke diesel turbo engine has been developed, with the hot surface of the porcelain ignition plug having a Pt wire wound around it. Current is only switched to the wire at low temperature and low load. Pressurised liquid H₂ is directly injected into the combustion chamber through eight flows, but only one flow at a time reaches the hot surface.

Novel Process for Direct Conversion of Free Energy of Mixing into Electric Power

J. JAGUR-GRODZINSKI and R. KRAMER, *Ind. Eng. Chem., Process Des. Dev.*, 1986, **25**, (2), 443-449

The direct conversion of salt gradients into electric power with the production of an acid and a base at the same time was examined. Devices combining features of an electrodialytic pile and those of fuel cells or of electrochemical half cells were designed. Electrodes were made by depositing Pt on active charcoal catalyst on a C cloth. Fuel cells used H₂O as the fuel, and air as the oxidant. Energy extracted from salinity gradients at power densities of up to 1W/m² of the membrane yields up to 0.6MW of electric power per m²/s of river or brackish water.

Graphoepitaxy of Platinum on Sawtooth Profile Gratings

K. KUSHIDA, H. TAKEUCHI, T. KOBAYASHI and K. TAKAGI, *Appl. Phys. Lett.*, 1986, **48**, (12), 764-766

The graphoepitaxies of Pt films on sawtooth profiles gratings have been examined by SEM. Pt was evaporated to different thicknesses onto (100)Si wafer gratings of 0.4 μm period. Pt films 100nm thick have crystallites of grain size of about one grating period wide and 0.5-5 μm long embedded in the gratings. Continuous films with (100) orientation are produced after further deposition and annealing.

Reliability of Germanium Avalanche Photodiodes for Optical Transmission Systems

H. SUDO, Y. NAKANO and G. IWANE, *IEEE Trans. Electron Devices*, 1986, **ED-33**, (1), 98-103

Over 600 Ge avalanche photodiodes (APD) for use in undersea optical transmission systems have been examined. The failure rates during high-temperature storage, high-temperature operation and surge endurance are discussed. The main failure of Ge-APDs was abnormal breakdown due to Al penetration from metallisations into Ge at temperatures above 200°C. When Au/Pt/Ti metallisations were used the Ge-APDs had excellent thermal stability.