

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

On the Homogeneity of Adsorption Centres and Catalysis on the Surface of Spongy Platinum

R. E. MARDALEISHVILI and E. V. KEROGU, *Dokl. Akad. Nauk SSSR*, 1987, **296**, (1), 154-157

Studies of the character of the distribution of active centres on the surface of spongy Pt of 99.99% purity were made in high vacuum of 10^{-7} torr. The results show that adsorption of H isotope on Pt occurs in isotopic volume, forming HD. In adsorption and desorption N_2 tests it was shown from limited saturation of the monolayer at -220°C that nearly half of the adsorbed H_2 can be desorbed and the other half can be removed from the surface at -196°C and higher. According to the data on the adsorbed molecular N_2 half the remaining molecules appear to be fixed with twice as many numbers of homogeneous surface centres, i.e. fixed on the surface more firmly than would be expected from irreversibility.

An Unusual State of Gold and Platinum on Some Fluoride Supports

G. D. KAZAKOVA, L. TH. KOMOLOVA, YU. S. MARDASHEV and V. V. NIKITIN, *Z. Phys. Chem. (Leipzig)*, 1987, **268**, (4), 666-672

The possible origins of the unusual state of Au(Pt) on some fluoride supports are discussed. The state is characterised by a negative shift in the binding energy of the electrons of the core level. The effect depends on the evolution of an acceptor band formed by Au(Pt) clusters in the forbidden band of the support, and the degree of the band expansion depends on the size of the interface region. The lamellar structure of the lattice of the supports, for AlF_3 or LaF_3 , or the size of ions, for BaF_2 , are likely to be promoting factors for increasing the interface region.

The Influence of Platinum Implantation on the Hydrogen Embrittlement of Tantalum

W. EDSINGER and G. K. WOLF, *Mater. Sci. Eng.*, 1987, **90**, 237-241

H embrittlement of Ta was studied under severe conditions so that the effect of implantation of Pt^+ ions to prevent the embrittlement could be found. The results show that metals such as Ta, Nb, Ti and Hf can be protected from H embrittlement in acids by implantation of metals, such as Pt, as long as the Pt is implanted only into the surface oxide layer and direct contact between the Pt and bulk metal is avoided. Damaged metal surfaces often become embrittled and in these cases implantation is especially helpful.

Redispersion of Pt/Alumina via Film Formation

I. SUSHUMNA and E. RUCKENSTEIN, *J. Catal.*, 1987, **108**, (1), 77-96

Alterations in the size of Pt particles on alternate heating in H_2 and O_2 in model Pt/ Al_2O_3 catalysts is reported. In O_2 the particles appear smaller, while on heating in H_2 they appear larger and extended. This contrasts with the usually observed extension of particles on oxidation and contraction on reduction. The change in size is explained by the formation of a detachable film—a "halo", or an undetectable film around each particle due to the strong interactions between crystallites and support in O_2 , and its withdrawal to merge with the respective particle in H_2 . The films remain close to and in contact with the parent particle and do not interconnect.

Adsorption-Induced Conductance Changes of Thin Pt Films and PtPd/TiO₂ Gas Sensors

A. G. SHASTRI and J. SCHWANK, *Appl. Surf. Sci.*, 1987, **29**, (3), 341-360

The chemisorption of H_2 and O_2 and the resulting changes in the electrical conductance of PtPd/TiO₂ and thin Pt films on glass were studied and compared. The activation energy of conduction increases as Pt film thickness decreases. H_2 chemisorption on thin Pt film causes an increase in conductance and in the activation energy of conduction. O_2 chemisorption results in a decrease in conductance and an increase in the activation energy of conduction. Compared to thin Pt films, relatively large changes in electrical conductance are observed upon chemisorption of gases onto PtPd/TiO₂. The electronic changes upon adsorption/desorption of gases are reversible for thin Pt films, but only partially reversible for PtPd/TiO₂.

Auger Electron Spectroscopy, X-Ray Photoelectron Spectroscopy, Work Function Measurements and Photoemission of Adsorbed Xenon on Thin Films of Pt-Re(III) Alloys

M. ALNOT, V. GORODETSKII, A. CASSUTO and J. J. EHRHARD, *Thin Solid Films*, 1987, **151**, (2), 251-262

AES, LEED, macroscopic work function measurements and the photoemission of adsorbed Xe(PAX) were used to investigate the deposition of 0-15 monolayers of Pt onto a Re(0001) single crystal, and also its subsequent annealing above 1000K. During deposition, the macroscopic work function reached the bulk value after deposition of 1 monolayer. The PAX and LEED studies indicated that Pt(III) grows epitaxially on Re(0001).

The Temperature Dependence of the Surface Composition of Pt-Rh Alloys

F. C. J. M. VAN DELFT, A. D. VAN LANGEVELD and B. E. NIEUWENHUYNS, *Surf. Sci.*, 1987, **189/190**, 1129-1134

AES was used to investigate the variation in surface composition of a polycrystalline Pt_{0.62}-Rh_{0.38} foil with the equilibrium temperature. An ultra clean surface exhibits a Pt enrichment which increases with increasing equilibration temperature from 80 to 89at.% Pt in the 800-1000K temperature range. At 1000-1500K an almost constant surface concentration of 89at.%Pt was found. The effect of P, C and Sn impurities is discussed. Pt enrichment in the surface and its temperature dependence are qualitatively in line with a model based on vibrational entropy contributions in addition to the enthalpy contributions used in classical surface segregation models.

¹⁹⁵Pt Knight Shift in the Heavy Fermion Superconductor UPt₃

Y. KOHORI, T. KOHARA, H. SHIBAI, Y. ODA, T. KANEKO, Y. KITAOKA and K. ASAYAMA, *J. Phys. Soc. Jpn.*, 1987, **56**, (7), 2263-2266

UPt₃ was observed by ¹⁹⁵Pt in both the normal and superconducting states. The ¹⁹⁵Pt Knight shift measurements were made by the spin-echo technique. The spectrum has a large negative shift and is quite anisotropic. At 5kOe no changes in the negative shift were observed down to 60mK, where the system was superconducting. Thus the conduction electron spin susceptibility does not decrease in the superconducting state. UPt₃ may still have anisotropic p-wave superconductivity.

Effect of Trapping on the Solubility and Diffusivity of Hydrogen in Palladium (α -Phase)

R. V. BUCUR, *J. Mater. Sci.*, 1987, **22**, (9), 3402-3406

The solubility and diffusivity data of H in Pd with different defect concentrations are discussed within the frame-work of the two-level model with local equilibrium (Oriani's model). Analytical expressions of the solubility isotherm and of the variation of the apparent diffusion coefficient depending on the total bulk concentration are derived. A good agreement is found between experimental results on the solubility and diffusivity of H₂ and the calculated values.

Phase Formation and Dissociation in the Thin-Film Pd/Al System

E. G. COLGAN, *J. Appl. Phys.*, 1987, **62**, (6), 2269-2274

Phase formation was studied for thin films in the systems Al/Pd, Pd₂Al/Al and Pd/PdAl/Al at 200-450°C. The films were prepared by sequential evaporation and co-evaporation, annealed under vacuum and analysed by Rutherford backscattering and X-ray diffraction. Pd₂Al₃ was found to be the dominant growing phase in the initial stages of the reaction for these samples, and Al was the dominant moving species during the formation of Pd₂Al₃.

Electrochemical Studies of TiO₂ Films with Various Palladium Implantation Profiles

J. W. SCHULTZE, L. ELFENTHAL, K. LEITNER and O. MEYER, *Mater. Sci. Eng.*, 1987, **90**, 253-262

Oxide covered Ti electrodes were implanted with various concentration profiles of Pd ions in order to investigate the radiation damage and the doping effect of ion implantation. The effects of doping and Frenkel defects could be separately assessed. A dominant influence of defect production increases in the order of the profiles: out<in<tot<through. For repassivation up to 2V high mobility defects migrate out of the film to form a new oxide of up to 0.2nm thick. The rate of electron transfer reactions increases in the order of profiles: out<in ≈ through<tot by several orders of magnitude. Thus the production of defects enhances the electron transfer reaction, but doping with Pd⁺ is most effective. Defects, energies and mobilities can be distinguished and the potential distributions can be estimated.

Diffusion during Ion Irradiation in Amorphous PdCuSi

J. BÖTTINGER, K. PAMPUS and B. TORP, *Europhys. Lett.*, 1987, **4**, (8), 915-919

Measurements of the tracer diffusion of Au in amorphous, melt-spun Pd₇₈Cu₄Si₁₆ have been carried out during low-flux ion irradiation to determine the effect of irradiation-induced defects on thermal diffusion in metallic glasses. The changes in the depth profiles of implanted Au due to diffusion were determined by Rutherford-backscattering spectrometry. Ion mixing was negligible. The irradiation enhances the diffusion. The temperature dependence of the diffusion is similar with or without irradiation.

Magnetic State of Hydrogenated Pd_{1-x}Fe_x Alloys

V. A. TSURIN, N. P. FILIPPOVA and A. P. STEPANOV, *Fiz. Tverd. Tela (Leningrad)*, 1987, **29**, (9), 2694-2698

The effect of the H content on the magnetic state of hydrogenated Pd_{1-x}Fe_x alloys was studied spectroscopically at 77-300K on samples prepared from roat.%Fe-Pd alloys hydrogenated either electrolytically in HCl or by saturation from gaseous H at 5-15 kbar and 250°C, followed by quenching at -20°C. The results showed that the transition of ferromagnetic-spinal glass can be realised by varying the H₂ content.

Effect of Ion Beam Mixing/Implantation at Low Temperature on Superconductivity in Palladium-Hydrogen and Palladium-Copper-Hydrogen Systems

H. LI, Z. DONG, F. YANG, R. WANG, J. LIU and W. GUAN, *Chin. Phys. Lett.*, 1987, **4**, (6), 241-244

The highest superconducting transition temperatures of 8.42 and 5.16K have been observed in the alloy systems Pd-H and Pd-Cu-H where the atomic ratios

$n = \text{H:Pd(Cu)}$ are 1 and 0.6, respectively. An ion beam bombardment at liquid He temperatures disorders the lattices and destroys the superconductivity.

Effect of Hydrostatic Pressure on the Magnetic Transition Temperature of MnRhAs

T. KANOMATA, K. SHIRAKAWA, H. YASUI and T. KANEKO, *J. Magn. & Magn. Mater.*, 1987, **68**, (3), 286–290

The effect of hydrostatic pressure on the magnetic order-order transition temperature, T_1 , and on the Curie temperature, was examined on powdered polycrystalline MnAsRh samples 10mm \times 1mm diameter, as the temperature was varied. Both variables increased with increasing applied pressure, and the pressure dependence of both was non-linear. The pressure derivatives of the transition temperatures at zero pressures were obtained. The transition entropy change at T_1 was calculated. The temperature variations of magnetisation and susceptibility are reported.

The Cu-Ir(Copper-Iridium) System

D. J. CHAKRABARTI and D. E. LAUGHLIN, *Bull. Alloy Phase Diagrams*, 1987, **8**, (2), 132–136, 195

An assessment of the Cu-Ir equilibrium diagram is presented. Thermodynamically the Cu-Ir system is not very different from the Cu-Rh system, in that a clustering effect predominates in both systems. Liquidus, solidus and solvus data are presented for temperatures from 500–2447°C. No metastable phases are reported, and crystal structure and lattice parameters are discussed. No thermodynamic measurements have been reported for Cu-Ir alloys, so a previously published equilibrium diagram has been utilised as a source of information for the different phases. It is suggested that the liquidus in the Cu-Ir system needs to be determined experimentally.

Phase Relations in the System Nickel-Copper-Sulphur-Ruthenium at 1200°C

J. NELL, *NTIS Chem.*, 1987, **87**, (41), 12–13

Dry sulphide experiments in the Cu-Ni-S-Ru system were performed at 1200°C to find the effect of Ru on the slow cooling of a UG-2-type matte. RuS₂, Ru metal and two Ru-Ni alloys were the only Ru bearing phases which were stable under the conditions. The resulting phase diagram indicates that a Ru-rich Ru-Ni alloy will co-exist with a sulphide liquid during the slow cooling of a Ru-rich UG-2-type matte.

Optical Properties of RuO₂ Thin Film

H. L. PARK, C. H. CHUNG, C. H. KIM and H. S. KIM, *J. Mater. Sci. Lett.*, 1987, **6**, (9), 1093–1094

The first transmission spectra of RuO₂ thin film were obtained using a Spex 1 m monochromator and transitions were assigned which showed good agreement with the theoretical calculations of Mattheiss. The thin film of RuO₂ was made on a slide glass substrate using vacuum evaporation. The deposition rate was 1

nm/s and the substrate was kept at 200°C. The thin film of RuO₂, \approx 50 nm thick, thus obtained was annealed at 400°C for 6h in a vacuum in order to obtain good crystallinity.

Corrosion of Ruthenium Dioxide Hydrate by Ce^{IV} Ions and Other Oxidants

A. MILLS, S. GIDDINGS and I. PATEL, *J. Chem. Soc., Faraday Trans. I*, 1987, **83**, (8), 3217–3229

A "test system" was devised to study the corrosion stability and O₂-catalytic activities exhibited by samples of RuO₂.xH₂O when exposed to strong oxidant, such as Ce^{IV} ions. The majority of the samples were unstable towards anodic corrosion, and showed only little O₂ catalytic activity (8% O₂ yield). The RuO₂.xH₂O samples prepared from oxide powder were highly hydrated. A minority of commercial RuO₂.xH₂O powders were found to be in a partially dehydrated form with resistance to corrosion.

CHEMICAL COMPOUNDS

Complex Platinum(II) Compounds with Purine and Pyrimidine Base and Their Nucleoside

A. I. STETSENKO, K. I. YAKOVLEV and S. A. D'YACHENKO, *Usp. Khim.*, 1987, **56**, (9), 1533–1563

A review is given of the synthesis, structure, physico-chemical properties and the reaction ability of complex Pt(II) compounds containing purine and pyrimidine bases and their nucleosides studied during the last 10 years. (216 Refs.)

The Structure of the New Quaternary Layered Material [Co_{1.5}Pt_{0.5}]Ta₆PtSe₁₆

S. A. SUNSHINE and J. A. IBERS, *J. Solid State Chem.*, 1987, **69**, (2), 219–223

Crystal structure studies of a new quaternary layered compound [Co_{1.5}Pt_{0.5}]Ta₆PtSe₁₆ found it crystallised in the monoclinic system with $a = 13.089(18)$, $b = 3.425(3)$, $c = 24.436(25)$ Å, $\beta = 104.9(1)^\circ$ with two formula units in the cell. The structure contains Ta atoms in both trigonal prismatic and octahedral sites, and Co atoms in a square-pyramidal environment.

Redox-Reactions Involving Low-Valence Complexes of Transition Metals: Phosphinecarbonyl Palladium and Platinum Clusters in the Synthesis of Binuclear Compounds

V. V. BASHILOV, E. G. MEDNIKOV, S. S. KURASOV, P. V. PETROVSKY, N. K. EREMENKO and V. I. SOKOLOV, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, (10), 2360–2362

The hetero-binuclear Pd and Pt complex PdPtCl₂(μ_2 -CO)(PPh₃)₃ was obtained by redox-addition of Pd₄(CO)₅(PPh₃)₄ and Pt₄(CO)₅(PPh₃)₄ clusters with MCl₂(PPh₃)₂ (where M = Pd, Pt) in benzene at 20°C. This unique isomer contains two PPh₃ ligands on a Pt atom.

Synthesis and Catalytic Properties of Protonated Palladium Carbonyl Phosphine Complexes

A. I. MIN'KOV, O. A. EFIMOV, N. K. EREMENKO and E. B. KLIMENKO, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, (9), 2076-2080

Studies of the reduction of Pd(OAc)₂ by CO in the system PPh₃-organic solution-HClO₄ showed formation of carbonyl hydrate Pd complex in the presence of n-butanol and formation of tris-(triphenylphosphine) Pd monohydrate during the reduction in acetone. Both obtained complexes catalyse reduction of nitrobenzene by CO.

Syntheses and Structures of Bis(thioether)-Bridged Rhodium Complexes and Their Catalytic Reactions with Alkynes

H. SONG, R. C. HALTIWANGER and M. RAKOWSKI DUBOIS, *Organometallics*, 1987, 6, (10), 2021-2028

The reaction of bis(ethylthio)methane(ETM) with Rh₂Cl₂(CO)₄ resulted in the formation of Rh₂Cl₂(CO)₂(ETM)₂(I). The reaction of (I) with triethylamine N-oxide resulted in the formation of Rh₂Cl₂(μ-CO)(ETM)₂(II). Both compounds were characterised by X-ray diffraction studies. Complexes (I) and (II) were found to serve as catalyst precursors for the cyclotrimerisation of terminal alkynes. Under a mixture of CO and acetylene at 1-2atm and 60-70°C in wet acetonitrile, complex (I) produced hydroquinone.

Late-Transition-Metal μ-Oxo and μ-Imido Complexes. I. μ-Oxo Complexes of Rhodium and Iridium

P. R. SHARP and J. R. FLYNN, *Inorg. Chem.*, 1987, 26, (19), 3231-3234

The synthesis, reactions and structures of Rh and Ir dppm (dppm = bis(diphenylphosphino)methane) A-frame μ-oxo complexes are reported. The oxo ligands are highly basic, this being unique to known oxo-complexes of late-transition metals, with reactivity patterns similar to those for O adatoms on late-transition-metal surfaces.

Synthesis and Spectroscopic Characterization of the Purple Tris(phenanthrene-quinone diimine)ruthenium(II) Ion

A. M. PYLE and J. K. BARTON, *Inorg. Chem.*, 1987, 26, (22), 3820-3823

The synthesis and spectroscopic characterisation of two new M(phi)_n complexes: [Ru(phi)₃]Cl₂ and Zn(phi)Cl₂ are reported. The complexes have novel spectroscopic features, and Ru(phi)₃²⁺ displays intense, unusual transitions at low energies. For the Ru(II) complex the aromatic exocyclic imine functionality leads to spectroscopic features that are sensitive to H bonding and may be characteristic of a delocalised charge-transfer framework. This Ru complex may be useful as a biophysical probe.

ELECTROCHEMISTRY

The Adhesion and Inhibitor Properties of Organic Coatings Investigated with Very Thin Polymer Films on Noble Metal Electrodes

K. DOBLHOFFER and I. EISELT, *Corros. Sci.*, 1987, 27, (9), 947-956

The electrochemical impedance and the rate of faradaic reactions were measured on Pt electrodes coated with a thin, 10⁻⁵cm, film of acrylonitrile glow-discharge polymer. The desorption of the organic matrix from the metal surface after immersion in 1M H₂SO₄ was determined. The rate of electrocatalytic charge-transfer reactions is directly proportional to the number of unblocked metal surface atoms, as determined from the H adsorption capacitance. It is concluded that the observed fraction of a metal surface accessible to the electrolyte and electrocatalytic activity is very relevant in the corrosion processes of coated metals.

Electrocatalytic Activity of Sulfur-Modified Platinum Electrodes: Selective Electrogenative Oxidation of Ethanol to Ethyl Acetate

S. H. LANGER and J. C. CARD, *J. Mol. Catal.*, 1987, 42, (3), 331-336

Ethyl alcohol can be converted to ethyl acetate selectively at a reduced SO₂-treated porous Pt black anode in an electrochemical cell which generates DC power. The cell has an acid electrolyte with an untreated porous Pt black/O cathode. The reaction may be general for the formation of esters from straight chain alcohols of 2C and higher. Secondary alcohols are selectively oxidised to ketones. For both oxidations, CO₂ formation is eliminated.

Highly Enhanced Anion Doping-Undoping Process at the Polypyrrole Electrode of Regulated Morphology Prepared with the Aid of Insulating NBR Film

K. NAOI and T. OSAKA, *J. Electrochem. Soc.*, 1987, 134, (10), 2479-2483

A polypyrrole (PPy) film grown with the aid of a pre-coated nitrile rubber (NBR) by an electropolymerisation method showed a highly enhanced anion doping-undoping process and a special electrode Pt/NBR/PPy was prepared. The guest polymer of PPy film grew through the fine channels etched by the penetration of the electrolyte into the NBR film during electropolymerisation and the host polymer of NBR film was subsequently removed to leave the backbones of the grown PPy film. Potential steps and AC impedance measurements for the electrodes showed that a Pt/NBR/PPy electrode has a faster anion doping process than a Pt/PPy electrode. A SEM study revealed that a PPy film formed with the aid of NBR polymer had a rough, porous and perpendicularly oriented structure.

Inner Resistance and Electrode Structure of the Bi-Facial-Dual Type Pt-SPE Membrane Electrode in the Hydrogen Oxidation and Oxygen Reduction

K. FUJIKAWA, H. ISHIKAWA, K. NARITA, A. YAMANAKA and R. ISHIDA, *Denki Kagaku*, 1987, 55, (8), 621-626
Electrochemical H oxidation and O reduction were studied on Pt-SPE (Solid Polymer Electrolyte) membrane electrodes, which were prepared by chemically plating Pt onto both sides of the various SPE membranes, and then used as gas-diffusion type electrodes. Linear I-V relationships were observed over almost the whole potential region. The apparent resistance, calculated from the slope, was deduced to arise from the transport of protons which dissociated from the sulphonic acid groups bonded to the Nafion molecules in the SPE matrix, and from the conductivity of the solution in the SPE. During polarisation of the electrode on the gas side, the potential of the electrode on the solution side was studied.

Laser-Processed Electrodes Consisting of Amorphous Nickel-Niobium-Platinum Group Metal Surface Alloys on Niobium

N. KUMAGAI, Y. SAMATA, A. KAWASHIMA, K. ASAMI and K. HASHIMOTO, *J. Non-Cryst. Solids*, 1987, 93, (1), 78-92

Laser processing was applied to bulk Nb substrates covered by electrodeposited Ni and platinum group metals in order to form amorphous surface alloys with excellent electrocatalytic activities. The Nb is alloyed to the electrodeposited metals by laser processing, hence the Nb content is determined by the laser process conditions. Nb contents must be 35-40at.% for vitrification. Overlapping traverses of the laser beam are necessary for vitrification of a wide area and often result in crystallisation in the heat-affected zone in the previously vitrified phase. Electrodes produced included Ni₄₀Nb₁Pd_{0.5}Rh on Nb; these alloys have excellent electrocatalytic properties on activation by HF solution, and they have a very high corrosion resistance during electrolysis of seawater.

Corrosion Behaviour of Surface Layers of Ti-Pd Alloy Obtained by Polyenergetic Implantation of Pd Ions into Ti

N. D. TOMASHOV, I. S. TASHLYKOV, O. A. ZHIL'TZOVA, G. P. CHERNOVA, M. I. GUSEVA and B. G. VLADIMIROV, *Zashch. Met.*, 1987, 23, (5), 791-795

Corrosion behaviour of surface layers of Ti-Pd alloy obtained by polyenergetic implantation of Pd ions into Ti was studied in 20% H₂SO₄ at 100°C. Studies were made of the dependence of the corrosion properties of Ti-Pd alloy surface on the character of Pd distribution in the Ti surface layers. The results showed that for the continuous support of Pd-Ti surface the passive state implanted Pd atoms acted not only as catalysts for the cathodic reaction, drawing out the H₂, but also as electron donors in the semi-conducting passivating oxides formed on the Ti surfaces in corrosion media.

PHOTOCONVERSION

Stabilization of Platinum-Loaded CdS Photocatalyst by Addition of EDTA

M. MATSUMURA, H. OHNISHI, K. HANAFUSA and H. TSUBOMURA, *Bull. Chem. Soc. Jpn.*, 1987, 60, (6), 2001-2003

Studies of the photocatalytic activity of Pd-loaded CdS powder in sulphite solutions showed it declined when illuminated over 2000h, and had half its initial activity at 600h. The photocatalyst stopped deteriorating on addition of a small amount (2mM) of ethylenediaminetetraacetic acid (EDTA) to the solution. The EDTA protects the Pt part of the photocatalyst from impurity metal deposition by forming stable metal-EDTA complexes in the solution. The reactivities of sulphite ions, EDTA and metal-EDTA complexes on illuminated CdS are examined electrochemically by use of CdS-sinter electrodes.

Thermal and Photolytic Reactions of Nitrosyl-Carbonyl Complexes of Rhodium and Iridium with Triphenylphosphine

M. KUBOTA, M. K. CHAN, D. C. BOYD and K. R. MANN, *Inorg. Chem.*, 1987, 26, (20), 3261-3264

The photolysis of [Rh(NO)(CO)(PPh₃)₂] in the presence of PPh₃ in dichloromethane resulted in the expulsion of NO rather than CO and the formation of trans-[Rh(CO)Cl(PPh₃)₂]. The thermal reaction and photoreaction of [Ir(NO)(CO)Cl(PPh₃)₂]BF₄(1) with PPh₃ leads to dissociation of NO and the formation of the Ir(II) radical [Ir(CO)Cl(PPh₃)₂]BF₄.

Visible Light Cleavage of Water by CdS Photoanode Coated with Polymer-Pendant Ru(bpy)₃²⁺ Film Containing RuO₂ Dispersions

M. KANEK, *Electrochim. Acta*, 1987, 32, (9), 1405-1407

The simultaneous formation of H₂ and O₂ by visible light cleavage of water was achieved using a CdS photoanode coated with polymer-pendant Ru(bpy)₃²⁺ film containing RuO₂ dispersions. The Ru complex worked as a relay to transport the holes formed on the CdS surface to the RuO₂ catalysts, where water oxidation takes place.

Photosensitised Reduction of CO₂ to CH₄ and H₂ Evolution in the Presence of Ruthenium and Osmium Colloids: Strategies to Design Selectivity of Products Distribution

I. WILLNER, R. MAIDAN, D. MANDLER, H. DÜRR, G. DÖRR and K. ZENGERLE, *J. Am. Chem. Soc.*, 1987, 109, (20), 6080-6086

The photoreduction of CO₂ to CH₄ and higher hydrocarbons occurs in aqueous solutions using visible light and Ru or Os colloids as catalysts. One system is composed of Ru(II)tris(bipyridine),

Ru(bpy)₃²⁺ as photosensitiser, TEOA as electron donor and a bipyridinium charge relay. Illumination gives CH₄ and C₂H₄, with H₂ evolution. A second system with Ru(II)tris(bipyrazine) as sensitiser, TEOA as electron donor and the Ru colloids forms CH₄, C₂H₄ and C₂H₆, with no H₂ evolution. H₂ evolution is inhibited by addition of bipyrazine, and CO₂ reduction is inhibited by thiols. CO₂ methanation by H₂ proceeds in the dark in the presence of Pt and Ru or Os colloids.

Formation of Oxygen from Water Photosensitised by (bpy)₂Ru[bpy(C₁₇)₂]²⁺ Built in Double-Ply, Lipid Membrane

E. I. KNEREL'MAN and YA. V. SHAFIROVICH, *Akad. Nauk SSSR, Kinet. Katal.*, 1987, **28**, (5), 1237-1239

A system is proposed which consists of a photosensitiser (bpy)₂Ru[bpy(C₁₇)₂]²⁺ built in a double-ply lipid membrane, acceptor K₂S₂O₈ electrons located in the outer solution and which is fixed on the membrane of a Co catalyst. The results showed the formation of O₂ under visible light irradiation with a quantum yield which reaches 20-40%.

A Molecular Water-Oxidation Catalyst Derived from Ruthenium Diaqua Bis(2,2'-bipyridyl-5,5'-dicarboxylic Acid)

F. P. ROTZINGER, S. MUNAVALLI, P. COMTE, J. K. HURST, M. GRÄTZEL, F.-J. PERN and A. J. FRANK, *J. Am. Chem. Soc.*, 1987, **109**, (22), 6619-6626

The controlled potential electrolysis of cis-Ru(II)L₂(OH)₂²⁺, where L is 2,2'-bipyridyl-5,5'-dicarboxylic acid in 0.5M H₂SO₄ solutions leads to the formation of a relatively durable and active molecular water-oxidation catalyst, which is an oxo-bridged dimer, L₂(H₂O)Ru-O-Ru(OH)₂L₂. The catalyst has been evaluated by various techniques. It is highly effective in mediating the thermal and visible-light-induced generation of O₂ from water. Carboxylic acid groups enhance catalytic activity and the durability of the dimeric complex.

ELECTRODEPOSITION AND SURFACE COATINGS

Investigation of the Influence of Pulse Parameters on Crack Formation in Palladium Electrodeposits

R. D. GRIMM and D. LANDOLT, *Surf. Coatings Technol.*, 1987, **31**, (2), 151-161

The current efficiency and the morphology of Pd deposits produced from an acid electrolyte on a rotating hemispherical electrode were investigated using DC, pulse plating and pulse reverse currents. Crack-free deposits were only obtained with pulse reverse current because co-deposited H was anodically oxidised during the reverse cycle. The current efficiency for Pd deposition decreased with the increasing ratio of anodic to cathodic charge.

On the Electronic Deposition of Shiny Coatings of Palladium-Cobalt Alloys for Electronics

W. DANOWA, M. AKEXANDROWA, M. GEORGIEWA and P. DINEFF, *Oberflaeche Surf.*, 1987, **28**, (9), 8-11

The properties of Pd alloys of corrosion resistance, hardness, excellent solderability, good optical properties and stability at high temperatures made Pd-Co and Pd-Ni suitable candidates for a study of coatings for use in electronics. Variables in the deposition process: electrolyte contents, Pd concentration, current density, temperatures, pH and the anodes used, were studied; and the structure of the coatings was then examined. Recommendations for electrolyte and deposition conditions are proposed.

Structure and Physio-Mechanical Properties of PdIn-Coatings

N. B. GORINA, E. V. ZYKOVA, G. S. BURKHANOV, V. F. SHATINSKIL, M. S. GOIKHMAN, V. S. KHLOMOV and E. A. VOITEKHOVA, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 1987, **23**, (8), 1315-1319

Pd-In alloy coatings containing 48, 50, 52, 54 and 56 at.% Pd were deposited on stainless steel substrates by a diffusion method (of deposition through solution alloy metals). Thus, single phase, homogeneous and solid PdIn coatings were obtained with high adhesion characteristics for all PdIn coatings with content variation of 1.5-2at.%. The driving force in the process appeared to be the concentration gradient which originated as the result of diffusion of metal components in the substrate.

Pulse and Periodic Reverse Current Plating of Palladium-Nickel Alloy

R. BOSHIN, W. FENGYIN and L. MING, *Nippon Kagaku Kaishi*, 1987, (8), 1593-1599

Pulse and periodic reverse current platings of Pd-Ni alloy were studied. The results showed that the pulse plating, and particularly the periodic reverse current plating improve the properties of Pd-Ni alloy deposits. The deposit obtained by periodic reverse current plating with a cycling period of 10-200ms, a ratio of cathode pulse current to anode reverse pulse current of 2-4, and a ratio of cathode pulse current on-time to anode reverse pulse current on-time of 0.5-5, is bright, smooth, compact and outstanding in corrosion resistance. The periodic reverse current plating was effective in decreasing grain size, smoothing surface and improving the deposit.

Pulse Plating of Palladium-Silver Alloys

O. DOSSENBACH, B. STURZENEGGER and J.-C. PUIPPE, *Oberflaeche Surf.*, 1987, **28**, (9), 16-22

The conditions leading to successful pulse plating of Pd-Ag alloys are discussed. The effects of experimental variables on the deposition which were examined include the Pd and Ag contents of their ammoniacal nitrate solutions and pulse parameters:- length of pulse, frequency and strength of pulse. The composition, hardness, ductility and specific resistance of the coatings were investigated.

The Electrolytic Deposition of Palladium-Silver Coatings from a Methylsulphonic Acid-Containing Electrolyte

R. J. LUO, F. FRIEDRICH and C. J. RAUB, *Galvanotechnik*, 1987, 78, (6), 1570-1572

The conditions used for the electrolytic deposition of Pd-Ag coatings from an electrolyte containing methylsulphonic acid were investigated, and the coatings produced were examined by an X-ray fine structure investigation. Effects of changes in temperature, current density, Ag and acid contents of the electrolyte were observed. Bright, fine grained coatings of Ag-Pd solid solutions containing 50-90 wt.% Ag were produced.

The Role of Additives in the Electrodeposition of Rhodium

N. KUBOTA, *Met. Finish.*, 1987, 85, (5), 55-57

The effect of the addition of $MgSO_4$ and K_2SeO_4 to Rh(III) sulphate solutions on the properties of electrodeposited Rh have been studied. When only Rh(III) sulphate was present grain size with random orientation grew at high current densities, and the surface of the deposit was partially non adherent. When Mg was added there was less distortion in the deposit and the potential of the Rh deposition became noble. Addition of Se made the potential less noble, and the grain size decreased, surface cracking was not present and there was less internal distortion, also adhesion and smoothing were promoted, thus enabling a thick deposit of Rh to be used.

APPARATUS AND TECHNIQUE

Thin Metal Film-Oxide-Semiconductor Structures with Temperature-Dependent Sensitivity for Unsaturated Hydrocarbons

F. WINQUIST and I. LUNDSTRÖM, *Sens. Actuators*, 1987, 12, (3), 255-261

Studies of metal-oxide-semiconductor structures with a thin (3-10nm) catalytic metal as the gate material, which are sensitive detectors for NH_3 gas, showed that the sensitivity for unsaturated HC for these structures can be considerably increased at elevated device temperatures. The sensitivities of different types of structures are compared. The ethylene sensitivity of a Pt thin film-oxide-semiconductor structure, operated at 190°C, was 1ppmv.

Low Power Thick Film CO Gas Sensors

D.-D. LEE, B.-K. SOHN and D.-S. MA, *Sens. Actuators*, 1987, 12, (4), 441-447

SnO_2/Pt thick film CO gas sensors were made by a screen printing method. The sensors were fired at 500-1000°C with a mixing ratio of Pt: SnO_2 of 0.2-1.0wt.%. The sensors showed a low operating temperature of ~100°C and high sensitivity to CO gas. The sensors fired at 600°C had the highest sensitivity when the SnO_2 :Pt ratio was 99.5:0.5 by wt. and response time of ~2s for 200ppm of CO.

Determination of Oxygen Activities in Highly Diluted Gas Mixtures Using a Solid-State Electrolyte Cell

H. J. CHRIST and H. G. SOCKET, *High Temp. Technol.*, 1987, 5, (3), 123-129

The applicability of an oxygen sensor using stabilised ZrO_2 as the solid-state electrolyte and catalytic Pt electrodes to measure O_2 activity in highly diluted gas mixtures was studied. It was found that the oxidation of CH_4 at Pt obeys a first order rate law. Due to the extremely low kinetics of the reaction, a slight reduction of $p(O_2)$ from the H_2/H_2O equilibrium value of the bulk gas occurred.

Palladium-Gate MOS Devices for Arsine Detection

W. MOKWA, K. DOBOS and G. ZIMMER, *Sens. Actuators*, 1987, 12, (4), 333-339

Studies on Pd-MOS structures, prepared with holes in the gate metal for detecting arsine, were performed in a flow system. The samples showed a reversible decrease of threshold voltage on admixture of arsine to an air stream at 350-470K. A change of threshold voltage of 34mV is found for 0.1ppm arsine in air ($T=433K$). For arsine concentrations of 2.5ppm, a response time of 40s and a recovery time of 300s are observed at 450K. The response of the same structures to small concentration of H_2 was also studied.

A Dual-Mechanism Solid-State Carbon-Monoxide and Hydrogen Sensor Utilizing an Ultrathin Layer of Palladium

K. W. JELLEY and G. J. MACLAY, *IEEE Trans. Electron Devices*, 1987, ED-34, (10), 2086-2097

Pd-gate MOS sensors were fabricated on p-type Si wafers. The gate Pd films were 25 and 40Å thick with an oxide thickness of 100Å. Voltage shifts in C-V curves and shifts in the Pd film impedance were measured as functions of CO and H_2 concentration with time as the gas ambient was varied. At room temperatures the devices were sensitive to H_2 , and to CO and H_2 at elevated temperatures. The 25Å Pd film was thick enough to give adequate electrical contact and porous enough to let the CO reach the Pd/ SiO_2 interface. On exposure to CO or H_2 the MOS capacitance and gate impedance both shifted. The impedance change may be due to the change in the potential between islands, which affects the quantum mechanical tunnelling.

Gas-Sensing Characteristics of Semiconducting Materials Based on In_2O_3 Depending on Composition Changes

K.-S. YOO and H.-J. JUNG, *Sens. Actuators*, 1987, 12, (3), 285-290

Gas-sensing materials for detecting flammable gases were developed by mixing In_2O_3 powder with one or two other chemicals such as SnO_2 , Y_2O_3 and Al_2O_3 , with a small addition of $PdCl_2$ as catalyst. Three compositions among the 15 tested showed the highest sensitivity to flammable gases; these were

49.5wt.%In₂O₃-50wt.%Al₂O₃-0.5wt.%PdCl₂, 20wt.%In₂O₃-29wt.%SnO₂-50wt.%Al₂O₃-1wt.%PdCl₂ and 40wt.%In₂O₃-9wt.%Y₂O₃-50wt.%Al₂O₃-1wt.%PdCl₂. Sensors based on the above compositions showed high sensitivity to CH₄, C₂H₆ and n-C₄H₁₀. They could detect down to a level of 1/20th of the lower explosion limits of each gas.

Sensing Behaviour of Pd-SnO_x MIS Structure Used for Oxygen Detection

W. P. KANG, J. F. XU, B. LALEVIC and T. L. POTEAT, *Sens. Actuators*, 1987, **12**, (4), 349-366

A new type of O₂ sensor with a Pd-SnO_x-Si₃O₄-SiO₂-Si-Al MIS structure was developed and is capable of detecting partial O₂ pressures of <0.1 torr at 300K. The detection principle of this device is based on the changes in ionic charge of the SnO_x film during O₂ adsorption and consequent changes in the flat-band voltage. The concentration of O ions adsorbed in the MIS structure at a given temperature and O₂ pressure are measured by the triangular voltage sweep method.

HETEROGENEOUS CATALYSIS

The Kinetics of Gas Phase Hydrogenation of Cyclohexene on Alumina-Supported Platinum in Static Reactor

O. ZAHRAA, S. H. AL KHOWAITER and E. AMMAR, *Arab Gulf J. Sci. Res., Math. Phys. Sci.*, 1987, **5**, (1), 21-35

The kinetics of cyclohexene hydrogenation over Pt/Al₂O₃ catalysts was studied in a static reactor at 303-373K, H₂ partial pressure of 40-220 torr and cyclohexene partial pressure of 20-80 torr. Cyclohexane was the only product observed and the rate of hydrogenation showed a maximum at 160 torr of H₂. The experimental results showed that the hydrogenation on Pt/Al₂O₃ catalysts proceeds via the associative mechanism.

Influence of Iridium Content on the Deactivation of Pt/Al₂O₃ Reforming Catalysts

J. BELTRAMINI and D. C. TRIMM, *Erdoel Kohle Erdgas Petrochem.*, 1987, **40**, (9), 400-403

The effect of Ir in Pt-Ir bimetallic catalysts was studied by investigating the activity, selectivity and stability of Pt, Ir and Pt-Ir catalysts used for methylcyclopentane reforming. Addition of Ir modifies the dehydrogenation capacity of Pt, reducing coke deposition and increasing the formation of lower molecular weight hydrocarbons by hydrogenolysis. The unwanted contribution from Ir is partially suppressed by coke deposition, which decreases the hydrogenolytic capacity and increases the production of aromatics. Ir also accelerates coke removal, and coke on the support may be removed by gas spillover from the metal. This action of Ir on Pt can be related to the assistance of bimetallic clusters on the Pt-Ir catalyst.

Effect of Platinum Content and Degree of Coking on the Properties of Platinum/Alumina Catalysts

B. B. ZHARKOV, V. L. MEDZHINSKII, L. F. BUTOCHNIKOVA, I. T. VALUEVA and V. B. MARYSHEV, *Neftekhimiya*, 1987, **27**, (4), 496-500

The effect of Pt content and degree of coking of 0.07-1.2wt.% Pt/ γ -Al₂O₃ catalysts on specific catalyst activity was studied during dehydrogenation of cyclohexane. Selectivity of butane hydrogenolysis, and also the rate of formation of carbonic deposits during conversion of the benzene fraction appeared to maximum degree in the area of low Pt surface coverage, at Pt contents of <~0.2wt.%.

Selective Liquid-Phase Hydrogenation of 2,6-Dinitrotoluene with Platinum Catalysts

O. M. KUT, F. YÜCELEN and G. GUT, *J. Chem. Technol. Biotechnol.*, 1987, **39**, (2), 107-114

The kinetics of the consecutive liquid-phase hydrogenation of 2,6-dinitrotoluene to 2-amino-6-nitrotoluene and 2,6-diaminotoluene were studied in ethanol with a 0.5% Pt/Al₂O₃ catalyst using a stirred tank slurry reactor, in the temperature and pressure range of 313-348K and 0.5-10MPa, respectively. The intrinsic kinetics of the consecutive reaction were described by a Langmuir-Hinshelwood type model. A maximum yield for the intermediate 2-amino-6-nitrotoluene of >95% was achieved when heat and mass transfer effects were eliminated.

Effect of Hydrogen Pressure on Dehydrocyclisation of n-Octane on Platinum/Alumina Catalysts

G. M. SEN'KOV, M. F. GORBATSEVICH and N. S. KOZLOV, *Dokl. Akad. Nauk BSSR*, 1987, **31**, (9), 815-817

Studies of the effect of H₂ pressure on the dehydrocyclisation of n-octane and the distribution of product aromatic hydrocarbons were studied on the Pt/Al₂O₃ and Pt+Cr/Al₂O₃ catalysts at 773K and 0.6-1.6MPa. Catalysts were prepared by saturation of Al₂O₃ by liquid ion solutions of H₂PtCl₆ and (NH₄)₂Cr₂O₇, followed by drying and reduction at 773K for 2h and contained 0.4-1.0wt.% of Pt and Cr. On both the studied catalysts, the yield of aromatic hydrocarbons decreased with the increase of H₂ pressure. The increase of H₂ pressure, during dehydrocyclisation of the n-octane, on both catalysts greatly affected the distribution of aromatic HC due to the specific effect of Cr on the activity of Pt/Al₂O₃ catalysts.

Variation of Catalytic Activity over PtRe/ γ -Al₂O₃

S. M. AUGUSTINE and W. M. H. SACTLER, *J. Phys. Chem.*, 1987, **91**, (23), 5953-5956

Hydrogen isotope exchange at 100°C and hydrogenolysis at 240°C were studied over γ -Al₂O₃ supported Pt, Re and a series of PtRe catalysts. Alloys behave as physical mixtures for the isotope-

exchange reaction. For hydrogenolysis, however, the PtRe catalysts behave differently than the Pt or Re monometallic catalysts. This is due to the formation of ensembles of atoms which contain both Pt and Re on the bimetallic catalysts and thus exhibit a heat of adsorption which is intermediate between the two. The most ensemble-specific reaction was total hydrogenolysis to methane. This rate was highest for sites on which adsorption is stronger than on Pt but weaker than on Re.

Pt/C Oxidation Catalysts. Part I. Effect of Carrier Structure on Catalyst Deactivation during the Oxidation of Glucose 1-Phosphate into Glucuronic Acid 1-Phosphate

H. E. VAN DAM, A. P. G. KIEBOOM and H. VAN BEKKUM, *Appl. Catal.*, 1987, **33**, (2), 361-372

Studies of the Pt-catalysed liquid phase oxidation of glucose 1-phosphate into glucuronic acid 1-phosphate showed a strong catalyst deactivation. This deactivation, which was caused by the presence of excess O₂ leading to a complete surface coverage and a distortion of the surface structure, was found to be preventable by the use of a catalyst carrier with particle geometry of a "built-in" diffusion barrier.

Colloidal Bimetallic Catalysts: Pt-Au

P. A. SERMON, J. M. THOMAS, K. KERYOU and G. R. MILLWARD, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, (9), 918-919

The bimetallic catalysts Pt_{100-x}Au_x (0 < x < 100) sols were prepared by reduction of the mixed aqueous solutions of H₂PtCl₆ and HAuCl₄ with a 1% trisodium citrate solution at 373K. The particles obtained from Pt_{100-x}Au_x sols are essentially purely crystalline, uniform in particle size and homogeneous. The Au content was found to affect the average particle size. The catalytic properties after adsorption on graphite resemble those of non-colloidal Pt-Au catalysts. However, a fine distinction of the properties was easy in the colloidal system.

Effect of Alumina-Deficiency and Promotion with Platinum and Rhenium on the Catalytic and Diffusional Behaviour of Mordenite Catalysts

A. K. ABOUL-GHEIT, M. F. MENOIFY, A. K. EL-MORSI and S. M. ABDEL-HAMID, *J. Chem. Technol. Biotechnol.*, 1987, **39**, (1), 37-43

Studies of the hydroconversion of n-heptane on Pt/HM, Pt/HM(AD) and Pt-Re/HM(AD) (AD = Al₂O₃-deficient; HM = hydrogen mordenite) catalysts in a continuous high-pressure plug reactor system were made by gas chromatography. The effectiveness factor, η , for each catalyst was calculated and the effect of diffusion on the catalytic behaviour was correlated. The η values obtained for n-heptane hydrogenation were found to be in the order: Pt-Re/HM(AD) > Pt/HM(AD) > Pt/HM. Catalysts showing larger η values have wider pores irrespective of their large metal loading.

Mechanism of Deuterium Addition and Exchange with Propene over Ni/SiO₂ and Pt/SiO₂ Catalysts at Low Temperatures

S. NAITO and M. TANIMOTO, *J. Chem. Soc., Faraday Trans. I*, 1987, **83**, (8), 2475-2486

The mechanism of the D₂ addition and exchange reaction of propene over Pt/SiO₂ and Ni/SiO₂ was studied by microwave spectroscopy and kinetic measurements. The associate mechanism prevails in the presence of gaseous D₂, while the dissociation mechanism operates in its absence. The results showed that terminal methylene carbon C₁ was most active over the Pt/SiO₂ catalyst, and isopropyl and n-propenyl species are the predominant intermediates.

Isomerisation of n-Hexane on Modified Platinum/Zeolite Catalysts

I. I. URBANOVICH, V. S. KOMAROV and L. P. SHIRIN-SKAYA, *Neftekhimiya*, 1987, **27**, (5), 634-637

Studies of the effect of additions of B, F and Sn on activity of Pt/zeolite Y type catalysts during isomerisation of n-hexane showed high catalytic activity and selectivity for Sn modified Pt/zeolite catalysts. The promoting effect depended on the nature of the addition. Hydrogenolysis of n-hexane decreased in the presence of Sn whereas the addition of B or F strengthened the hydrocracking activity of the catalysts. The most selective were catalysts containing Ce, B and Sn.

Complete Catalytic Oxidation of Volatile Organics

J. J. SPIVEY, *Ind. Eng. Chem. Res.*, 1987, **26**, (11), 2165-2180

A review is given of the heterogeneous catalytic oxidation of volatile organic compounds (VOC's) in the presence of (among others) platinum group metals. Emphasis is placed on reviewing the fundamental scientific principles general to all catalytic oxidation reactions and then showing how the reported works have been applied to the control of VOC's at conditions of interest. The parameters for this review are 25-400°C and atmospheric pressure. (125 Refs.)

Benzene Hydrogenation over Supported and Unsupported Palladium. I. Kinetic Behavior. II. Reaction Model

P. CHOU and M. A. VANNICE, *J. Catal.*, 1987, **107**, (1), 129-139; 140-153

The kinetics of benzene hydrogenation were examined over unsupported Pd powder and Pd supported on Al₂O₃, TiO₂, SiO₂, C, SiO₂-Al₂O₃ and zeolite under a wide range of reaction conditions. A modified Langmuir-Hinshelwood model is proposed to describe the behaviour. The activity of all samples showed a temperature-dependent maximum at near 495K, but unsupported Pd had a greater tendency to deactivate. The lowest turnover frequencies occurred on Pd powder, while values 10-50 times higher occurred over low-temperature reduced Pd catalysts using Cl-containing precursors and acidic supports.

High Pressure Syngas Reaction over Pd/SiO₂ Catalyst – Effects of Fe and Ag Addition to Pd/SiO₂ on Catalytic Behavior

H. ARAKAWA, T. HANAOKA, O. NISHIDA, A. IGARASHI, K. TAKEUCHI, T. MATSUZAKI and Y. SUGI, *Shokubai*, 1987, 29, (6), 458–461

Methanol synthesis from syngas over Fe- and Ag-modified Pd/SiO₂ catalysts was investigated. CO conversion over Fe/Pd/SiO₂ increased gradually when Fe was added, but adding Ag decreased the CO conversion in the atomic ratio range Ag:Pd=0–0.1. Ag and Fe had little influence on methanol selectivity.

Effect of the Composition of Palladium-Containing Y Type Zeolites on Their Catalytic and Acidic Properties during Alkylation of Isobutene with Ethene

M. A. TIMURZIEVA, S. N. CHADZHIEV, V. L. BAIDURSKII and I. L. ALEXANDROVA, *Neftekhimiya*, 1987, 27, (4), 501–505

Catalytic and acidic properties of PdHY, PdCaY, PdLaY, PdHR.E.Y (Rare Earth=R.E.), and PdHCaR.E.Y type zeolites were studied during alkylation of isobutene with ethene. The PdHCaR.E.Y zeolite catalyst was the most active yielding iso-paraffins C₈ with very high selectivity. The acidity of the catalysts was studied by thermosorption of NH₃ and the effect of substituted cations on the catalytic properties is explained.

A Highly Active Catalyst for the Oxidation of Carbon Monoxide, Prepared from Amorphous Palladium-Zirconium Alloy

A. BAIKER, D. GASSER and J. LENZNER, *J. Chem. Soc., Chem. Commun.*, 1987, (23), 1750–1751

The successful application of an amorphous Pd, Zr, alloy for the preparation of a highly active catalyst for CO oxidation is reported. The amorphous Pd₁Zr₂ used as catalyst precursor was prepared from a premixed melt of the pure metals by rapid quenching using the technique of melt spinning. The results showed that in situ activation of an amorphous Pd, Zr, alloy leads to a Zr supported Pd catalyst with activity for CO oxidation of more than one order of magnitude higher than a similar catalyst prepared by impregnation of ZrO₂ with a (NH₄)₂PdCl₄ salt.

Study of the Support Evolution through the Process of Preparation of Rhodium/Lanthana Catalysts

S. BERNAL, F. J. BOTANA, R. GARCIA, F. RAMIREZ and J. M. RODRIGUEZ-IZQUIERDO, *J. Chem. Soc., Faraday Trans. I*, 1987, 83, (8), 2279–2287

The evolution undergone by the support throughout the processes involved in the preparation of lanthana-supported Rh catalysts was studied by spectroscopic and thermal techniques. A Rh/LaO(OH) catalyst was obtained by a reduction process at 623K. Reduction temperatures of ≤ 723 K are necessary to prepare the Rh/La₂O₃ catalysts.

Promoter Effect of Iron on Olefin Hydroformylation Catalyzed by SiO₂-Supported Rhodium-Iron Bimetallic Carbonyl Clusters: Rh-Fe³⁺ Bimetallic Activation of Catalytic CO Insertion

A. FUKUOKA, M. ICHIKAWA, J. A. HRILJAC and D. F. SHRIVER, *Inorg. Chem.*, 1987, 26, (22), 3643–3645

Rh-Fe bimetallic carbonyl clusters have been used as molecular precursors for the preparation of Rh-Fe bimetallic catalysts. The derived Rh-Fe³⁺ species are highly active for migratory CO insertion, as observed by the rates of the hydroformylation of ethylene and propylene, which are dramatically enhanced.

Reaction Mechanism for Selective Synthesis of Gasoline-Range Isoalkanes from Syngas over RuPtHY Zeolites. II. Role of Metals and Acid Sites

Y.-G. SHUL, Y. ARAI, T. TATSUMI and H. TOMINAGA, *Bull. Chem. Soc. Jpn.*, 1987, 60, (7), 2335–2341

The roles of metals and acid sites were studied during the selective synthesis of gasoline-range isoalkanes from syngas catalysed by Ru-Pt/zeolite Y. Alloying Ru with Pt enhanced 1-octene conversion as well as CO conversion. Reaction of 1-octene over metal-free dealuminated HY zeolite produced cracking products with high selectivity for isobutanes which could be possibly due to acid-catalysed reactions on zeolites.

HOMOGENEOUS CATALYSIS

Transition Metal Promoted Reactions of Polyhedral Boranes and Carboranes

L. G. SNEDDON, *Pure Appl. Chem.*, 1987, 59, (7), 837–846

The use of platinum group metal catalysts to catalyse or promote a variety of transformations involving polyhedral boranes and carboranes, including borane-acetylene addition, acetylene-borane insertion, borane-olefin coupling, dehydro-coupling, dehydrocondensation and cage-growth reactions is demonstrated. Selected examples which illustrate the scope and possible mechanisms of these reactions are discussed.

Effect of SnCl₂ on Activity and Selectivity of Pd(II) Complexes in Catalytic Reaction of Hydrocarboxylation of Olefins

E. S. PETROV, A. V. PROPCHENKO, L. F. STAROSEL'SKAYA and M. I. TEROKHOVA, *Zh. Obshch. Khim.*, 1987, 57, (8), 1802–1806

Studies of the effect of SnCl₂ on the catalytic activity of PdCl₂(PPh₃)₂ complexes were made during hydrocarboxylation of 1-heptene to dioxane. The addition of SnCl₂ to the PdCl₂(PPh₃)₂ complex increased the rate of production of caprylic acid and thus slowed down the production of its isomer. This resulted in a considerable increase in the selectivity of the products of the hydrocarboxylation reaction towards a linear structure.

Palladium-Mediated Silylation of Organic Halides with Disilane/F-Reagent

Y. HATANAKA and T. HIYAMA, *Tetrahedron Lett.*, 1987, **28**, (40), 4715-4718

The Pd(PPh₃)₄ catalyst was used in the promotion of tris(diethylamino)sulfonium trimethyldifluorosilicate in the reaction of vinyl halides with hexamethyldisilane to yield corresponding vinyl silanes in good yields chemoselectively and stereospecifically. The reaction conditions were so mild that it is possible to introduce trimethylsilyl moiety to thermally labile substrates.

Selectivity Studies on the Hydroformylation of Propylene Catalysed by the Cluster Anion [HRu₃(CO)₁₁]⁻

G. SÜSS-FINK and G. F. SCHMIDT, *J. Mol. Catal.*, 1987, **42**, (3), 361-366

The chemo- and regioselectivity of the hydroformylation of propylene catalysed by [NEt₃][HRu₃(CO)₁₁]⁻ was studied as a function of solvent, temperature and pressure. The catalyst was chemospecific and independent of the reaction conditions. Aldehydes only were formed. The regioselectivity could be optimised by varying the reaction conditions. For the best result the n:i ratio of the butanals formed was as high as 98.6:1.4. The catalyst remained unchanged in the solution in all cases.

FUEL CELLS

Corrosion in Low and High Temperature Fuel Cells - An Overview

A. J. APPLEBY, *Corrosion (Houston)*, 1987, **43**, (7), 398-408

The corrosion rates of cathode components and Pt catalysts in the four principal types of electrolyte fuel cells are discussed. Corrosion ultimately limits the life of the fuel cell and its performance. Corrosion in phosphoric acid fuel cells using Pt cathode catalysts is discussed. Any increase in their efficiency can only be achieved by increasing the cathode potential.

GLASS TECHNOLOGY

Investigation of Platinum Alloys for Melting of Inclusion Free Laser Glass: Final Report

T. IZUMITANI, H. TORATANI and H. E. MEISSNER, *NTIS Mater. Sci.*, 1987, **87**, (41), 5

The suitability of Pt alloys: Pt-Ir, Pt-Rh, Pt-Au, ZGSPt, ZGSPt-Au and ZGSPt-Rh, compared to Pt as crucible materials for melting LHG-8 phosphate laser glass was investigated. The tendency of forming metallic inclusions and the ionic dissolution of alloy components in the glass were compared for all the materials. The various ways by which platinum may be introduced into the glass melt have also been examined.

ELECTRICAL AND ELECTRONIC ENGINEERING

A Comparative Study of Phase Stability and Film Morphology in Thin-Film M/GaAs Systems (M = Co, Rh, Ir, Ni, Pd, and Pt)

T. SANDS, V. G. KERAMIDAS, K. M. YU, J. WASHBURN and K. KRISHNAN, *J. Appl. Phys.*, 1987, **62**, (5), 2070-2079

Reproducible and stable contacts to compound semiconductor devices were produced from thermodynamically stable phases after the reaction of metals with the compound semiconductor. The final phases produced by the reactions between GaAs and thin metal films of Pt, Rh, Pd, Ir, Co and Ni were studied. They were identified as MGa for M = Pt, Pd, Rh, Ni and Co, monoarsenides of Co and Ni, diarsenides of Pt, Pd, Rh and Ir and Ir₃Ga₅. The spectroscopic, microscopic and X-ray diffraction analyses of the products of thin-film M/GaAs reactions reveal the distribution, grain size and crystallographic texture of these end phases.

Effects of Interfacial States on the Capacitance-Voltage Characteristics of Pd/SiO₂/n-Si Schottky Diodes

P. E. BAGNOLI and A. NANNINI, *Solid-State Electron.*, 1987, **30**, (10), 1005-1012

The shape of the 1/C² vs. reverse voltage characteristic of an MIS device with an ultrathin insulating layer was theoretically examined. To test the predictions 1/C²/V curves of Pd/SiO₂/n-Si MIS Schottky diodes were measured under N₂ and in two H₂/N₂ mixtures, and compared with Pd/n-Si curves. Changes of slope and the appearance of non-linear behaviour observed in hydrogenated devices are interpreted in terms of interactions between H atoms and interface states. Pd-gate MIS structures could be used to observe the effects of interfacial states on the electrical properties of the SiO₂/n-Si interface.

Control of Electrical Properties of RuO₂ Thick Film Resistors

T. INOKUMA and Y. TAKETA, *Act. Passive Electron. Components.*, 1987, **12**, (3), 155-166

The effects of adding various amounts of oxides of elements, such as Cu, Co, Ta, La, Mn, Ti, Ta, Mn, Sb, V, Mo, Fe, W, etc., and glass to the electrical properties of RuO₂ thick film resistors are discussed. Each oxide caused one of four effects, namely, to reduce the resistivity substantially and to shift the TCR considerably in the positive direction, to increase the resistivity substantially and to shift the TCR considerably in the negative direction, to have little effect on resistivity and to shift the TCR in the negative direction, or to have little effect on either resistivity or on the TCR. For a few additives added simultaneously the effects are the sum of effects of individual oxides. It is thus possible to manufacture RuO₂ thick film resistors with resistivity and TCR close to the value required.