

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

High Temperature Oxidation of Pt-45Pd-10Rh

G. W. GRAHAM, T. J. POTTER, W. H. WEBER and H. S. GANDHI, *Oxid. Met.*, 1988, 29, (5/6), 487-497

Following earlier studies of oxidation-induced compositional changes on the surface of Pt-Rh and Pd-Rh foils, the surfaces of Pt-45Pd-10Rh foils have now been examined after oxidation at 875-1075K, in 20%O₂-Ar at atmospheric pressure. A thin surface layer of mainly PdO formed at the lower temperatures, and pure PdRhO₂ at 1075K.

The Effect of Cr and W Nucleation Layers on the Magnetic Properties of CoPt Films

J. K. HOWARD, *J. Appl. Phys.*, 1988, 63, (8), 3263-3265

Alloy films of CoPt are of interest for use as recording media in high-density longitudinal recording technology. With the aim of improving magnetic properties, Co₈₀Pt₂₀ films were deposited onto 1000Å thick layers of Cr, CrV alloy and W. Significantly higher coercivity values, of 2415 Oe, were observed on the W/Co₈₀Pt₂₀ composite, compared to 1925 Oe for CrV/Co₈₀Pt₂₀.

Detection of Short- and Long-Range Order in Cu-Pt Alloys

J. BANHART, W. PFEILER and J. VOITLÄNDER, *Phys. Rev. B*, 1988, 37, (11), 6027-6029

Short-range order (SRO) and long-range order (LRO) were studied in Cu-Pt alloys at various temperatures and compositions by means of the electrical resistivity measurements. Stable long-range-ordered equilibrium states can be achieved by thermal treatment. The effects of SRO and LRO can be separated for the non-equiatomic compositions by examining the resistivity change on SRO and LRO.

Disordering and Recrystallisation of Pt-Ni-Cu Alloys

O. N. OGORODNIKOVA, V. S. LITVINOV, A. A. KURANOV and YU. G. KARPOV, *Fiz. Met. Metalloved.*, 1988, 65, (5), 967-969

The temperatures of recrystallisation and disordering of Pt₃₀Ni_{30-x}Cu_x (x=0, 3, 5, 10, 15 and 25at.%) alloys were measured by differential and resistometric analysis at 300-750°C. The results showed that regulating the annealing of these Pt alloys after plastic deformation does not eliminate its after effect, and heating of the disordered alloy is followed by recrystallisation. The position of temperature intervals in these processes and the effect of heat on the disordered alloy depended on the Cu concentration.

Concentration Changes of Pt and Si in a Pt/Poly-Si Thin Layer System between 750 and 1000°C

G. L. P. BERNING and C. W. LOUW, *Appl. Surf. Sci.*, 1988, 31, (4), 420-425

A Pt/polycrystalline Si/SiO₂/Si(100) multilayer system was prepared and annealed at 750°C in order to grow a PtSi layer on the polycrystalline Si layer. Upon subsequent annealing at 820°C the unreacted polycrystalline Si diffused partly into the PtSi. When equilibrium was reached at 880°C, the polycrystalline Si and PtSi layers were almost completely separated with the Si nearer to the surface. After annealing at 1000°C for 10 min, the Pt and Si concentrations were constant throughout the top layer.

Interdiffusion in Platinum-Tin Oxide Multilayered Films

T. SUZUKI, T. YAMAZAKI and T. YOKOI, *J. Mater. Sci., Lett.*, 1988, 7, (6), 669-670

The interdiffusivity of polycrystalline Pt-SnO₂ multilayered films with an interplanar distance λ of ~3.5nm was investigated after the films were formed. X-ray diffraction patterns after annealing at different temperatures and for different times provided 9×10^{-22} cm²/s at 500°C for the interdiffusivity.

Phase Equilibria in the RuO₂-Bi₂O₃-PdO System

M. HROVAT, S. BERNIK and D. KOLAR, *J. Mater. Sci., Lett.*, 1988, 7, (6), 637-638

The phase equilibria in the title system were investigated because of possible reactions between the components during manufacture of thick film resistors. Phase diagrams for PdO-RuO₂, PdO-Bi₂O₃, RuO₂-Bi₂O₃ and the ternary system are presented. There was no ternary compound. The tie lines are between PdO-Bi₃Ru₃O₁₁ and Bi₃Ru₃O₁₁-Bi₂PdO₄. The results show that there is no reaction between the conductive phase in thick film resistors (either RuO₂ or Bi ruthenate) and PdO during the firing of thick film circuits.

Critical Behaviour of Amorphous Gd_{0.70}Pd_{0.30}H_{0.20}

D. J. GRIFFITHS, G. GOLD, B. BOUCHER and R. TOURBOT, *J. Phys. F*, 1988, 18, (5), 993-1000

The magnetisation of amorphous Gd_{0.70}Pd_{0.30}H_{0.20}, which was prepared by sputtering, was measured at 100 and 300K in fields of up to 5kOe. While the Curie temperature, T_c, was much lower than that observed for undiluted liquid-quenched amorphous Gd_{0.70}Pd_{0.30}, the magnetic response in low fields was identical, indicating that the critical behaviour of the amorphous system does not change upon H addition.

Decoupled Bulk and Surface Crystallization in Pd₈₅Si₁₅ Glassy Metallic Alloys: Description of Isothermal Crystallization by a Local Value of the Avrami Exponent

A. CALKA and A. P. RADLIŃSKI, *J. Mater. Res.*, 1988, 3, (1), 59-66

The isothermal devitrification of Pd₈₅Si₁₅ amorphous alloys was studied by differential scanning calorimetry and XRD. The crystallisation of aged samples starts from the surface and proceeds several micrometers into the bulk, producing a layer of strongly textured Pd(111) followed by a mixture of Pd₂Si, Masumoto MSI phase and untextured Pd. The crystallisation occurs via a different (bulk) mechanism, resulting in a mixture of Masumoto MSI phase and untextured Pd. The bulk mechanism is the only one observed in as-quenched samples. The observed variation of the Avrami coefficient, *n*, with the crystallised volume fraction, *x*, is explained by a change in nucleation rate during devitrification.

Evidence from Hydrogen Solubility Studies for Ordering in Hypostoichiometric Alloys of Pd₃Mn

A. CRAFT, R. FOLEY, T. B. FLANAGAN, K. BABA, Y. NIKI and Y. SAKAMOTO, *Scr. Metall.*, 1988, 22, (4), 511-515

Pd-Mn alloys were prepared and H solubilities at various temperatures for the quenched form of each alloy were measured. Ordering in the alloys, electrical resistance behaviour, H solubilities and electron diffraction patterns were obtained as the alloys were put through various cooling regimes. There are abrupt increases in the H solubility and electrical resistance as quenched samples of hypostoichiometric Pd₃Mn are heated. This is attributed to ordering of the alloy matrix. Low temperature H solubility comparisons of quenched and slowly cooled alloys show large differences, which support the fact that ordered forms exist. The electron diffraction patterns indicate that the order is of the Ag₃Mg type, which is found in Pd₃Mn after annealing in vacuo.

Physical Properties of Icosahedral and Glassy Pd-U-Si Alloys

P. GRÜTTER, H. BRETSCHER, G. INDLEKOFER, H. JENNY, R. LAPKA, P. OELHAFEN, R. WIESENDANGER, T. ZINGG, H.-J. GÜNTHERODT and J.-B. SUCK, *Mater. Sci. Eng.*, 1988, 99, 357-360

Various physical properties were measured on glassy, crystalline and quasicrystalline samples of the Pd-U-Si system. Large differences are observed between the static structure factors of the quasicrystalline and glassy samples; however, their dynamic properties are nearly identical but quite different from those of the fully crystallised samples. The general features of the valence electron structure of the quasicrystalline phase are very similar to those of the corresponding glassy alloy, and similar intensities at the Fermi energy are observed. The electrical resistivity, the Hall coefficient and the magnetic susceptibility have been measured to high temperatures.

On the Stability of the Ordered Pd₄V Phase in a Proton-Irradiated Pd-15at.%V Alloy

J. CHENG and A. J. ARDELL, *J. Less-Common Met.*, 1988, 141, (1), 45-53

The maximum temperature at which the ordered Pd₄V phase forms in a Pd-15at.%V alloy irradiated by 400 keV protons was found between 350 and 420°C. Annealing studies after irradiation showed that Pd₄V is most probably a thermodynamically stable equilibrium phase with a critical ordering temperature slightly below 400°C. Interstitial dislocation loops are prevalent in the microstructure of samples irradiated at 200°C, whereas more widely extended stacking fault ribbons are commonly observed at irradiation temperatures of 420°C. The diameters of the loops were smaller at 200°C than at 350°C. The segregation of preferential V atoms to these defects causes the preferential formation of Pd₄V in regions between them.

CHEMICAL COMPOUNDS

Rhodium and Iridium Oxometallates—A New Class of Solid Microporous Materials

A. R. SIEDLE, R. A. NEWMARK, W. B. GLEASON, R. P. SKARJUNE, K. O. HODGSON, A. L. ROE and V. W. DAY, *Solid State Ionics*, 1988, 26, (2), 109-117

Organometallic Keggin ion complexes, [(Ph₃P)₂Rh(CO)]₄SiW₁₂O₄₀ and [(Ph₃P)₂IrH₂]₄P₂W₁₂O₄₀ have been characterised by solid state NMR and X-ray absorption spectroscopy. They constitute a new class of chemically microporous solids, and show how large molecular metal oxide clusters can form extensible lattices in which co-ordinatively unsaturated organometallic cations can be stabilised and studied. In some cases these cations are mobile and form bimetallic species. Reactions involving olefin isomerisation, hydroformylation, hydrogenation, dehydrogenation and C-H activation are described.

ELECTROCHEMISTRY

Adsorption and Oxidation of Methanol and Formic Acid on Platinised Platinum Modified with Tin Adatoms

M. A. STITSYN, A. N. ZHUCHKOV, V. N. ANDREEV and V. E. KAZARINOV, *Elektrokhimiya*, 1988, 24, (5), 686-690

The kinetics of adsorption and oxidation of methanol and formic acid on a platinised Pt electrode modified with Sn adatoms was studied in solutions of CH₃OH, HCOOH and H₂SO₄ at potentials of 0.2-0.4V by potentiodynamic impulse and radioactive indicator methods. Adsorption of methanol resulted in the formation of a COH product and also produced higher oxidised HC particles. In static conditions, the proportion of these adsorbed particles increases with an increase in the number of Sn adatoms on the electrode. The dependence of the rate of electro-oxidation of HCOOH on H₂ is confirmed.

The Electrochemical Reactivity of Toluene at Porous Pt Electrodes

J. ZHU, TH. HARTUNG, D. TEGMEYER, H. BALTRUSCHAT and J. HEITBAUM, *J. Electroanal. Chem. Interfacial Electrochem.*, 1988, **244**, (1 and 2), 273-286

The electroreduction and electro-oxidation of toluene adsorbed on Pt electrodes were studied spectrometrically. Part of the toluene starts to desorb at the potentials where H₂ adsorption begins. At potentials below 0.1V, hydrogenation to methylcyclohexane also occurs. Adsorbed intermediates which are in a higher oxidation state than toluene are also formed, and can only be oxidised in subsequent sweeps.

High Temperature Water Electrolysis: The Cathodic Process at the Cermet (Pt + La_{0.8}Sr_{0.2}CrO₃)/Zirconia Interface

G. B. BARBI and C. M. MARI, *Solid State Ionics*, 1988, **26**, (3), 240-250

Studies were made of the kinetics of the reduction of steam at the interface between a Pt containing cermet and an yttria stabilised zirconia electrolyte to find the effect of 30wt.%Pt embedded in the cermet. The presence of an outer porous Pt layer deposited onto the underlying cermet layer resulted in a great increase of the kinetic parameters of the overall reaction. However, the presence of metallic Pt embedded in the structure of the mixed oxide layer, restricted the section available for diffusion of reducible species.

The Effect of Palladium on Hydrogen Absorption and Mobility in AISI 4130 Steels

F. FONDEUR, T. A. MOZHL and B. E. WILDE, *Corros. Sci.*, 1988, **28**, (5), 461-470

The effect of Pd in solid solution on the H absorption and mobility in AISI 4130 steels was studied by cathodic polarisation and H permeation techniques in 1N NaOH. Pd additions resulted in a higher H permeation rate due to an increased diffusivity and a decreased H trapping effect. No significant differences were observed in the cathodic polarisation parameters as a result of these Pd additions, showing the effect of Pd is a bulk metallurgical effect. The work shows that Pd segregates to potential H traps and subsequently repels H from these sites.

Electrocatalytic Oxidation of Formic Acid on Pd + Pt Alloys of Different Bulk Composition in Acidic Medium

A. PAVESE, V. SOLIS and M. C. GIORDANO, *J. Electroanal. Chem. Interfacial Electrochem.*, 1988, **245**, (1 and 2), 145-156

The electroadsorption and oxidation of formic acid on two Pd + Pt alloys of different bulk composition were studied and compared to values taken on pure metals. The HCOOH dehydrogenative adsorption is faster on Pd sites, but the strongly adsorbed intermediate is formed only at Pt sites, irrespective of the Pd atom neighbourhood. The synergistic effect observed with the alloys is time and potential dependent.

Electrochemical Reduction of Nitrate and Nitrite in Concentrated Sodium Hydroxide at Platinum and Nickel Electrodes

H.-L. LI, D. H. ROBERTSON and J. Q. CHAMBERS, *J. Electrochem. Soc.*, 1988, **135**, (5), 1154-1158

The electrochemical reduction of nitrite and nitrate in concentrated NaOH solution at Pt, Ni and platinised Ni electrodes was studied as a function of electrode material, temperature and solution composition. Electrolysis of NaNO₃ in 3M NaOH + 0.25M Na₂CO₃ at 80°C on platinised Ni cathodes resulted in high current efficiency for the overall electrode reaction, a five-electron reduction to N₂. NH₃ is formed in constant current electrolyses at high current densities. The presence of O in the cathode compartment increased the rate of nitrate reduction under these conditions. Voltammetric studies showed that electrode reaction involves surface phenomena and is not mass transfer controlled. Maximising current efficiency for producing N₂ or NH₃ gas can have much significance for treating radioactive waste solutions.

Electrooxidation of Methanol on Platinum Bonded to the Solid Electrolyte, Nafion

A. ARAMATA, T. KODERA and M. MASUDA, *J. Appl. Electrochem.*, 1988, **18**, (4), 577-582

The electro-oxidation of methanol was enhanced on binary electrodes PtSn-SPE, PtRu-SPE and PtIr-SPE (SPE is a solid polymer electrolyte, Nafion) in H₂SO₄ solution, when compared with the activity of Pt-SPE, which is known to have a higher activity than a Pt electrode. This dual enhancement of the oxidation rate for PtSn-SPE and PtRu-SPE catalysts is due to the modification of the oxidation state of Pt by Sn and Ru and to the presence of H₂O and CH₃OH, both modified by the SPE matrix. This modification appears to weaken their H bonds in solution. The PtIr-SPE catalyst had enhanced catalytic activity compared to Pt or Ir. This is discussed in terms of Ir oxidised at relatively low positive potentials, assisting the redox process of Pt⁰/Pt²⁺ or Pt²⁺/Pt⁴⁺ in the SPE matrix.

Characteristics of Platinum Group Metal Anodes Prepared by Thermal Decomposition Method

T. MURANAGA, *Denki Kagaku*, 1988, **56**, (2), 117-123

The Ti/Pt-IrO₂ anode showed low Cl and high O₂ overvoltage characteristics. PdO can be used as the diluent of IrO₂ in the Ti/Pt-IrO₂ anode, as long as the IrO₂ content in the anode is kept over 15%. The Ti/Pt-IrO₂(30) and Ti/Pt-IrO₂(20)-PdO(10) anodes showed high current efficiency in a chlorate cell and a diaphragm cell compared to Ti/TiO₂-RuO₂(30mol%) anode. The use of the anode made of thin layer TiO₂/Pt-IrO₂(30) layer improved durability to Na-amalgam cathode. A modified Ti/Pt-IrO₂(30) anode was effective for maintaining high current efficiency in ion-exchange membrane cells because of low Cl and optimum O₂ overvoltage.

Effect of Phosphates on the Corrosion and Electrochemical Behaviour of Ruthenium-Titanium Oxides Anodes and Ruthenium Dioxide

M. M. PECHERSKII, S. V. EVDOKIMOV, L. E. CHUVAEVA, N. YA. BUNE and V. V. GORODETSKII, *Elektrokhimiya*, 1988, **24**, (6), 850-853

The effect of phosphates on the corrosion and electrochemical behaviour of Ru-Ti oxide electrodes and RuO₂ was studied in various pH and NaCl concentrations at 87°C, and at anodic current density of 0.2 A/cm². The electrodes contained 30 mol % RuO₂, 70 mol % TiO₂ (4.5 g Ru/m²) and RuO₂ (26 g Ru/m²). The phosphate ions which adsorbed on Ru-Ti oxide anodes and on RuO₂ decreased the corrosion rate, and O₂ was exposed on the anodes, without any substantial overloading of the Cl reaction. It is suggested that the addition of small amounts of phosphate may increase the stability of the anodes.

Spontaneous Oxidation of Water to Oxygen by the Mixed-Valence μ -Oxo Ruthenium Dimer L₂(H₂O)Ru^{III}-O-Ru^{IV}(OH)L₂ (L = 2,2'-bipyridyl-5,5'-dicarboxylic Acid)

M. K. NAZEERUDDIN, F. P. ROTZINGER, P. COMTE and M. GRÄTZEL, *J. Chem. Soc., Chem. Commun.*, 1988, (13), 872-874

The mixed-valence μ -oxo Ru dimer of the title converted spontaneously into L₂(H₂O)Ru^{III}-O-Ru^{III}(H₂O)L₂ with simultaneous oxidation of H₂O to O₂ at a very low thermodynamic driving force of the reaction, of <0.1 eV per transferred electron. The unique feature of this complex is that the catalytically active state is accessible at very low overvoltage. This behaviour is unprecedented in homogeneous H₂O oxidation catalysis. The finding could be useful in modelling the processes occurring on the surface of catalysts, such as colloidal RuO₂, and represents great progress in the development of artificial analogues of the green plant H₂O splitting enzyme.

PHOTOCONVERSION

The Photocatalytic Activity of a Platinized Titanium Dioxide Catalyst Supported over Silica

K. DOMEN, Y. SAKATA, A. KUDO, K.-I. MARUYA and T. ONISHI, *Bull. Chem. Soc. Jpn.*, 1988, **61**, (2), 359-362

The effects of different loadings of platinized TiO₂ on the photocatalytic activity of H₂ evolution from aqueous methanol over Pt-TiO₂/SiO₂ catalysts was studied. The optimum calcination temperature for catalytic activity was at 998 K. For all the catalysts studied there was an optimum Pt loading for the amount of TiO₂ present which gave maximum H₂ evolution. The activity for H₂ evolution decreased with the decrease in the amount of supported TiO₂/SiO₂, that is, with increase of dispersion.

The Structure of cis- and trans-Dichloroethenes Adsorbed on Pt(111). Photochemical Reactions of cis- and trans-1,2-Dichloroethene Adsorbed on Pd(111) and Pt(111)

V. H. GRASSIAN and G. C. PIMENTEL, *J. Chem. Phys.*, 1988, **88**, (7), 4478-4483; 4484-4491

The structures and photochemical behaviours of cis-1,2- and trans-1,2-dichloroethene (DCE) adsorbed on Pd(111) and Pt(111) surfaces were studied by EELS and TDS at 110-300 K. For multilayer coverage on either metal surface, irradiation of physisorbed DCE at 110 K with broad band irradiation ($\lambda > 200$ nm) results in photoisomerisation, cis \rightleftharpoons trans. For monolayer coverage on Pt(111) at 110 K, photolysis of chemisorbed DCE resulted in loss of the two Cl atoms to form a single HC product, chemisorbed acetylene. The study indicates that photochemistry of molecules chemisorbed on a metal surface is possible despite the proximity of the conducting surface.

Photoelectrochemical Characterization of Novel Rhodium Iodide Photoconductors

M. W. PETERSON and B. A. PARKINSON, *J. Electrochem. Soc.*, 1988, **135**, (6), 1424-1431

The photoelectrochemical and physical properties of three Rh iodides, which form a new class of semiconducting and photoconductive materials, is reported. Crystalline and amorphous RhI₃ and especially the previously unreported RhI_{4.1-4.3} (RhI₄) have been prepared and examined. The former are semiconductors with bandgaps in a range useful for photovoltaic and photoconductive devices. The structure of the latter material is predicted to be a chain of edge-sharing Rh iodide octahedra, where variations in preparation change the chain lengths and hence the electrical and photoelectrochemical properties. Large areas of thin film amorphous RhI₃ and RhI₄ are readily fabricated, which may make them attractive as photoconductors for, say, xerography.

Dehydrogenation of Saturated Hydrocarbons by Photocatalysis Using Carbonyl (halogeno) phosphine - Rhodium Complexes

K. NOMURA, H. KUMAGAI and Y. SAITO, *Shokubai*, 1988, **30**, (2), 204-207

Remarkably high photocatalytic activities of the title Vaska-type Rh complexes RhX(CO)(PR₃)₂ (X = halogen, PR₃ = tert-phosphine), were observed for alkane dehydrogenation, yielding alkene and H₂. The wavelength and photointensity dependence studies showed that the trico-ordinate species RhX(PR₃)₂, which were photogenerated under excitation conditions, are responsible for the catalysis cycle of alkane dehydrogenation with no photoassistance despite the thermodynamic difficulty. This catalyst design increases the concentration of catalytically-active species for C-H bond splitting.

APPARATUS AND TECHNIQUE

Quasi-Static and High Frequency C(V)-Response of Thin Platinum Metal-Oxide-Silicon Structures to Ammonia

T. FARE, A. SPETZ, M. ARMGARTH and I. LUNDSTRÖM, *Sens. Actuators*, 1988, **14**, (4), 369-386

Thin film Pt-gate MOS capacitors are of interest as possible NH₃ gas-sensitive devices. The effects of NH₃ exposure on the high frequency and quasi-static capacitance-voltage characteristic of Al and Pd Pt-MOS capacitors are discussed. There is a decrease in NH₃ sensitivity with decreasing Pt film thickness; this is related to the high impedance of the film and probably also to its microstructure.

Slow Quenches of High-Quality Single Crystals of Platinum and Palladium

A. KHELLAF, R. M. EMRICK and J. J. VUILLEMIN, *Phys. Rev. B*, 1988, **37**, (12), 6717-6722

A new technique for growing and quenching high-purity, low-dislocation-density Pt and Pd single crystals is developed. This technique traps at least 87% of the vacancy concentration at 90% of the melting point without significantly increasing the dislocation density during the quench. It produces high quality single crystals with a controllable supersaturation of vacancies for study by various techniques, without significant background signals.

Effect of Heat Treatment on Physical Properties of Pt-Based Alloy Wires for High Temperature Strain Gauge Application

B.-Z. FENG and D.-X. LI, *Metal*, 1988, **42**, (7), 669-671

The effects of heat treatments on the resistivity, temperature coefficient of resistance, tensile strength, rate of elongation, elastic modulus, linear expansivity, etc., on Pt-W and Pt-W-Re alloy wires used as sensors in high temperature strain gauges have been investigated. The optimum process for Pt-W involved solution heat treatment at 1000°C for 1 minute followed by water quenching and holding at 720°C for 30 hours; for Pt-W-Re the optimum treatment was 1000°C for 1 minute, followed by water quenching, then stable treatment at 820°C for 30 h.

Thin Palladium Films Prepared by Metal-Organic Plasma-Enhanced Chemical Vapour Deposition

E. FEURER and H. SUHR, *Thin Solid Films*, 1988, **157**, (1), 81-86

A simple, low temperature method for the deposition of Pd films using allylcyclopentadienyl Pd complex is reported. In this organic plasma-enhanced CVD process bright metallic films can be produced at low temperatures producing films of pure Pd or composites with a wide range of electrical conductivity. The resistivity of these films approaches that of bulk Pd. If O₂ is the carrier gas, the films are PdO.

Hydrogen Permeation through a Thin Film of Palladium: Influence of Surface Impurities

R. LALAUZE, P. GILLARD and C. PIJOLAT, *Sens. Actuators*, 1988, **14**, (3), 243-250

The influence of the surface state of a thin Pd film on H₂ diffusion was investigated to improve the reliability of a Pd-MOS H₂ sensor. Surface states of the sample were analysed by a temperature programmed technique; C, S and O could affect H energetic adsorption sites and thus the gas permeation process through the membrane.

Ru(bipy)₃Cl₂ Luminescence as Optical Step Signal for Detector Testing

K. BRETTEL and E. SCHLODDER, *Rev. Sci. Instrum.*, 1988, **59**, (4), 670-671

The use of picosecond-laser-flash-induced luminescence of the dye tris-(2,2'-bipyridyl)Ru(II)chloride as an optical step signal for testing the time response of fast optical detection systems is discussed. Following excitation at any wavelength between 250 and 550 nm, a single emission band between 570 and 700 nm is displayed which decays monoexponentially with a lifetime of ~600 ns in deoxygenated solution at room temperature.

HETEROGENEOUS CATALYSIS

The Role of Chlorine in the Regeneration by Hydrogen of Coked Reforming Catalysts

A. PARMALIANA, F. FRUSTERI, A. MEZZAPICA and N. GIORDANO, *J. Catal.*, 1988, **111**, (2), 235-242

The effect of surface Cl on the regeneration of several coked Pt/γ-Al₂O₃ honeycomb reforming catalysts has been investigated. Regeneration tests were performed at 400°C, after the dehydrogenation of methylcyclohexane, in a continuous flow microreactor. A catalyst with ~0.5% Cl shows complete regeneration during static and dynamic H₂ treatments, which is attributed to a maximum in the H₂ spillover from Pt to Al₂O₃, which restores the catalyst surface, freeing it of hydrocarbon residues.

Effect of Sulphur on the Dehydrocyclisation of n-Hexane, n-Hexene and n-Heptane on Reforming Catalysts

M. WILDE, R. STOLZ, R. FELDHAUS and K. ANDERS, *Chem. Tech. (Leipzig)*, 1988, **40**, (5), 208-211

Studies of the effect of S pretreatment on the conversion of n-hexane, n-hexene and n-heptane over Pt/Al₂O₃, Pt-Re/Al₂O₃ and Pt-Re-Cr/Al₂O₃ catalysts were made at atmospheric pressure. The presulphidation stabilised the activity and selectivity of dehydrocyclisation and resulted in high yields of H₂ and liquid product. After repeated use Re containing catalysts without presulphidation became similar to sulphided ones, and after reactivation with CCl₄ in air high activity was obtained.

Dispersion and Catalysis of Platinum in Bimetal/Zeolite Catalysts

H. J. JIANG, M. S. TZOU and W. M. H. SACTLER, *Appl. Catal.*, 1988, **39**, (1-2), 255-265

The effects of modifier elements, such as Fe^{2+} , both under oxidising and reducing conditions, on the formation of Pt particles in NaY zeolite, and the implication of these interactions for the ultimate dispersion and catalytic activity of these Pt particles were studied. The unreduced transition metal ions interact chemically with the Pt metal particles. The interaction appears to make use of the incompletely filled d orbitals of both Pt and anchoring ion. The modifier ions can block smaller cages during calcination, stabilise Pt^{2+} ions during and/or after calcination, and after reduction they can anchor Pt particles on the zeolite supports. The Pt/FeNaY zeolite catalysts exhibited higher activities for benzene hydrogenation and n-hexane hydrogenolysis than Pt/NaY, but the activity for methylcyclopentane (MCP) hydrogenolysis was lower for Pt/FeNaY. Catalysis of Pt/NaY was similar to that of Pt/SiO₂, but the ring opening selectivity of MCP is different, due to geometric constraints.

The Effect of Electrochemical Oxygen Pumping on the Steady-State and Oscillatory Behaviour of CO Oxidation on Polycrystalline Pt

I. V. YENTEKAKIS and C. G. VAYENAS, *J. Catal.*, 1988, **111**, (1), 170-188

The effect of electrochemically pumping O^{2-} to or from a porous polycrystalline Pt catalyst film used for CO oxidation at atmospheric pressure and 250-600°C was studied. The Pt acted as a catalyst and as an electrode in the solid electrolyte cell CO, O₂, Pt/ZrO₂(8 mol% Y₂O₃)/Pt, O₂. The pumping had a dramatic non-Faradaic effect; the steady-state reaction rate increases or decreases by a factor of 2, but a 500% increase in reaction rate is observed under severely reducing conditions. Reaction rate oscillations can be induced or stopped by adjusting the rate of O^{2-} transfer and thus the electrode potential.

Isomerization of Ethylbenzene and m-Xylene on Zeolites

Y. S. HSU, T. Y. LEE and H. C. HU, *Ind. Eng. Chem. Res.*, 1988, **27**, (6), 942-947

The simultaneous isomerisation of ethylbenzene and m-xylene on zeolite catalysts, including Pt/mordenite, Pt/USY, Pt/ZSM-5 and Pd/ZSM-5 has been studied. Pt/ZSM-5 was the best catalyst; Pd/ZSM-5 was better than Pt/USY, although both are good enough for the reactions compared with Pt/mordenite. The transformation of m-xylene to o- or p-xylene may be limited by the mass-transfer rate of the diphenylmethane-type intermediate, and the formation of o-xylene from ethylbenzene may be restricted by the smaller protonated cyclopropane intermediate. The ratio p-xylene : o-xylene is increased with temperature, and is in the order: Pt/USY < Pd/ZSM-5 = Pt/ZSM-5.

Genesis and Characterization of Transition Metal Clusters in Y Zeolites

W. M. H. SACTLER, M. S. TZOU and H. J. JIANG, *Solid State Ionics*, 1988, **26**, (2), 71-76

The size and location of Pt particles in Y zeolites largely depend on the calcination conditions following ion exchange. Calcination destroys NH₃ ligands and promotes migration of Pt ions from supercages to sodalite cages. Reduction then results in small Pt clusters in supercages, but large Pt particles form at the external surface if all the Pt ions are located in sodalite cages. When Pt ions are present in comparable quantities in both types of cages, those in the supercages are reduced at low temperature, and act as nucleation sites for Pt atoms leaving the sodalite cages at higher temperatures. By filling sodalite cages with auxiliary ions of other transition elements, the migration of Pt ions into such cages can be suppressed and higher Pt dispersion is obtained after reduction.

Liquid-Phase Hydrogenation of Butadiene in the Presence of Palladium Based Catalysts

P. S. IVANOV, A. V. NOVIKOVA, O. P. PARENAGO, KH. DIMITROV and V. M. FROLOV, *Neftekhimiya*, 1988, **28**, (3), 320-323

Studies of the mechanism of the liquid-phase hydrogenation of butadiene in the presence of 0.05-1wt.%Pd/ γ -Al₂O₃ catalysts showed a yield of butane at >90% selectivity. The Pd/ γ -Al₂O₃ catalysts are characterised by maximum activity during hydrogenation, with less tendency to run a similar reaction of butene isomerisation.

Remarkable Activity Enhancement of Rh/Al₂O₃ Prepared from RhCl₃ for CO-H₂ Reaction by the Pretreatment of High Temperature Evacuation

H. FUJITSU, H. ISHIBASHI and I. MOCHIDA, *Chem. Lett. Jpn.*, 1988, (4), 581-583

Studies of the catalytic activity of Rh/Al₂O₃, prepared from RhCl₃, for the CO-H₂ reaction at 473 and 523K showed a remarkable enhancement by evacuation after the reduction of the catalyst. Evacuation at 773K after reduction with H₂ at 673K increased the activity of Rh/Al₂O₃ to a maximum of 1200 mmol CO/g Rh h, comparable to that of Rh/TiO₂.

Molecular Design of Heterogeneous Catalysts by Using Metal Cluster Complexes—Their Structures and Catalytic Properties

M. ICHIKAWA and A. FUKUOKA, *Shokubai*, 1988, **30**, (2), 168-171

Studies of bimetal cluster-derived catalysts prepared using SiO₂-supported Rh₄Fe₃, Rh₃Fe, Ir₄Fe, Pd₆Fe₆ carbonyl clusters and NaY(NaX) zeolite-entrapped RhFe and Rh_{6-x}Ir_x carbonyl clusters as the precursors showed very high activities and selectivities for C₁-C₂ alcohol production in the CO+H₂ reaction, and higher alcohols in hydroformylation.

Oxygen Transfer between Rhodium and an Oxygen-Ion Conducting Support

I. S. METCALFE and S. SUNDARESAN, *AIChE J.*, 1988, **34**, (6), 1048-1050

Highly dispersed Rh catalysts prepared on γ -Al₂O₃ and YSZ (yttria stabilised zirconia) supports were studied during automobile CO-NO exhaust conversion. The results showed that for CO oxidation, Pt/YSZ and Rh/YSZ outperform Pt/Al₂O₃ and Rh/Al₂O₃, respectively, even under excess CO conditions. This is due to the YSZ support introducing an additional pathway for bringing O₂ to the catalytic sites. The presence of H₂O vapour increased the rate of the CO-NO reaction over both catalysts. The Rh/YSZ catalyst was found to be superior to the Rh/Al₂O₃ catalyst under both wet and dry reaction conditions.

Effect of Particle Microstructure on Alkane Hydrogenolysis on Rh/SiO₂

S. GAO and L. D. SCHMIDT, *J. Catal.*, 1988, **111**, (1), 210-219

Oxidation of Rh/SiO₂, followed by low-temperature reduction in H₂, produces hydrogenolysis activities for the catalyst which are up to 10⁵ times higher than after high-temperature annealing in H₂. The alteration in activity is larger for larger particle sizes and for C₂H₆ than for C₃H₈ or C₄H₁₀. Freshly oxidised catalyst produces more CH₄, while annealed catalyst produces larger alkanes. Activation in O₂ begins at 25°C, and H₂O is effective in partially activating the catalyst.

Lanthana-Promoted Rh/SiO₂. II. Studies of CO Hydrogenation

R. P. UNDERWOOD and A. T. BELL, *J. Catal.*, 1988, **111**, (2), 325-335

The influence of lanthana promotion on CO hydrogenation over Rh/SiO₂ was studied, and it was found that promoted catalysts exhibited higher turnover frequencies for the synthesis of CH₄, C₂-C₄ hydrocarbons, CH₃OH and C₂ oxygenates than unpromoted Rh/SiO₂. The turnover frequency for each product goes through a maximum with increasing lanthana addition. Selectivity for CH₃OH, C₂ oxygenates and C₂-C₄ hydrocarbons formation is also increased, while selectivity for CH₄ is decreased. Infrared observations show that lanthana promotion blocks the chemisorption of CO onto surface Rh sites, and also indicates acyl, formate and acetate groups on the catalyst surface.

Ethane Hydrogenolysis on a Ru(1,1,10) Surface

C. EGAWA and Y. IWASAWA, *Surf. Sci.*, 1988, **198**, (1/2), L329-L334

An investigation of the hydrogenolysis of ethane on a Ru(1,1,10) stepped surface has shown the steady state reaction rates to be one or two orders of magnitude higher than on supported catalysts. Active sites for the reaction are step sites composed of low coordination number surface atoms.

HOMOGENEOUS CATALYSIS

Bulk Ruthenium as an HDN Catalyst

A. S. HIRSCHON and R. M. LAINE, *Energy & Fuels*, 1988, **2**, (3), 292-295

A series of Group VI to Group VIII bulk metals was tested for HDN (the catalytic removal of N) activity by using a solution of tetrahydroquinoline in *n*-hexadecane. The results showed that bulk Ru is exceptionally effective for C-N bond cleavage at temperatures as low as 200°C and H pressures of 500 psig. Under similar conditions, Rh and Pt were less active, and Os, Ni, Mo and Re were inactive.

Hydrogenation of Dehydroamino Acid Derivatives in the Presence of Palladium(II) Complexes with Methionine

I. N. LISICHKINA, A. I. VINOGRADOVA, M. B. SAPOROVSKAYA, V. K. LATOV and V. M. BELIKOV, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, (5), 1170-1172

Studies of the catalytic activity of Pd(II) complexes with R- and S-methionine reduced by H₂ or NaBH₄ showed that the catalytic system formed during the interaction, complexes S- (or R)-MetHPdCl₂, had high catalytic activity for the hydrogenation of industrial cinnamic acid, but the enantioselectivity of this reaction was only 3-3.4%. The hydrogenation of N-acetyldehydrophenylalanyl-S-tyroline in presence of R- and S-MetHPdCl₂ yielded products with a diastereometric surplus of 18-24% R-S-isomer.

Formation Mechanism and Structure of Compounds Catalytically Active in Propylene Dimerization and Formed in Pd(acac)₂-PR₃-BF₃OEt₂ Systems

V. S. TKACH, F. K. SCHMIDT, G. V. RATOVSKII, N. D. MALAKHOVA, N. A. MURASHEVA, M. L. CHERNYSHEV and O. V. BURLAKOVA, *React. Kinet. Catal. Lett.*, 1988, **36**, (20), 257-262

Ultraviolet and ¹H NMR spectroscopic studies were performed of the interaction between the components of the catalytic system Pd(acac)₂-PR₃-BF₃OEt₂ during the dimerisation of propylene to linear hexenes with 59% selectivity. A formation mechanism for active [R₃P-Pd-H]⁺BF₄⁻ compounds is suggested.

Rhodium(II) Acetate Catalyzed Reactions of 2-Diazo-1,3-Indandione and 2-Diazo-1-Indanone with Various Substrates

M. J. ROSENFELD, B. K. RAVI SHANKAR and H. SHECHTER, *J. Org. Chem.*, 1988, **53**, (12), 2699-2705

Decomposition of 2-diazo-1,3-indandione (1) by Rh(II) acetate (2) in cyclohexane and in benzene results in overall C-H insertion to give 2-substituted 1,3-indandiones. Anisole, (1) and (2) yield 2-(4-methoxyphenyl)-1,3-indandione (74%); benzenes substituted by single methyl or halogen groups yield the corresponding ortho- and para-substitution products. Spirocyclopropanes are obtained by Rh(II)-catalysed additions of (1) to olefins; electron deficient olefins do not give adducts.

Oxygen Evolution by Means of Water Oxidation Catalyzed by Mononuclear Ruthenium-Ammine Complexes

M. KANEKO, R. RAMARAJ and A. KIRA, *Bull. Chem. Soc. Jpn.*, 1988, **61**, (2), 417-421

Mononuclear Ru-ammine complexes, $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$ and $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$, have been found to catalyze O_2 evolution from H_2O using Ce(IV) as an oxidant, under homogeneous and heterogeneous conditions. The water oxidation process depends on the ionic strength of the medium. Higher acidic conditions gave higher O_2 amounts. Heterogeneous catalysis using the Ru complex in Kaolin was as effective as homogeneous catalysis.

Competitive Cyclopropanation and Cross-Metathesis Reactions of Alkenes Catalyzed by Diruthenium Tetrakis Carboxylates

A. F. NOELS, A. DEMONCEAU, E. CARLIER, A. J. HUBERT, R.-L. MÁRQUEZ-SILVA and R. A. SÁNCHEZ-DELGADO, *J. Chem. Soc., Chem. Commun.*, 1988, (12), 783-784

Observation of an efficient, competitive reaction pathway between carbene-transfer and alkene metathesis, promoted by a Ru-based system, is reported for the first time. The addition of ethyl diazoacetate to a mixture of styrene and norbornene containing a catalytic amount of $\text{Ru}_2(\text{OAc})_4$ promoted both the cyclopropanation and a selective cross-metathesis of the alkenes.

FUEL CELLS

Oxygen Reduction at $\text{Pt}_{0.65}\text{Cr}_{0.35}$, $\text{Pt}_{0.2}\text{Cr}_{0.8}$ and Roughened Platinum

M. T. PAFFETT, J. G. BEERY and S. GOTTESFELD, *J. Electrochem. Soc.*, 1988, **135**, (6), 1431-1436

Oxygen reduced in 0.5M H_2SO_4 at the two named alloys and at the roughened surfaces produced by selective depletion of Cr has been investigated using conventional electrochemical techniques, and it is concluded that the increase in O_2 reduction reaction current measured on roughened rotating disc electrode surfaces is due only to the increase in Pt surface area. Data presented demonstrate the benefit of increasing the surface area of these Pt electrodes.

Advances in Solid Polymer Electrolyte Fuel Cell Technology with Low Platinum Loading Electrodes

A. SRINIVASAN, E. A. TICIANELLI, C. R. DEROUIN and A. REDONDO, *J. Power Sources*, 1988, **22**, (3 & 4), 359-375

The Gemini Space program showed the first major application of fuel cell systems. This paper presents methods to advance fuel cell technology by: (1) use of low Pt loading ($0.35\text{mg}/\text{cm}^2$) electrodes, (2) optimisation of anode/membrane/cathode interfaces by hot-pressing, (3) pressurisation of reactant gases (most important when air is used as cathodic reactant), and (4) adequate humidification of reactant gases.

Oxygen Electrodes for Rechargeable Alkaline Fuel Cells

L. SWETTE and J. GINER, *J. Power Sources*, 1988, **22**, (3 & 4), 399-408

Progress is reported on the investigation and development of electrocatalysts and supports to be used for the positive electrode of moderate temperature, single unit, rechargeable alkaline fuel cells. To date PbPdO_2 , CdPd_3O_4 , Bi_2PdO_4 , $\text{Pb}_2(\text{Ir}_{2-x}\text{Pb}_x)\text{O}_{7-y}$, $\text{Pb}_2(\text{Ru}_{2-x}\text{Pb}_x)\text{O}_{7-y}$, $\text{Na}_x\text{Pt}_3\text{O}_4$ and also Co tetramethoxyphenylporphyrin have been prepared and evaluated as electrocatalyst materials.

ELECTRICAL AND ELECTRONIC ENGINEERING

Effects of Processing Conditions on the Characteristics of Platinum Silicide Schottky Barrier Diodes

D. MOY, S. BASAVAIHAH, C. T. CHUANG, G. P. LI, E. HACKBARTH, S. B. BRODSKY and M. R. POLCARI, *Solid-State Electron.*, 1988, **31**, (5), 843-849

A study was performed of the effects of various processing conditions on the formation of PtSi Schottky barrier diodes. The interaction between PtSi and the contact metallurgy during subsequent annealing was also studied. The results show that oxide etching by wet etch is probably incomplete, leaving residues or suboxides on the surface of Si substrates which interfere with the subsequent PtSi formation.

Relations between Electrical Properties of RuO_2 Thick Film Resistors and Glass Viscosity

O. ABE, Y. TAKETA and M. HARADOME, *Denki Kagaku*, 1988, **56**, (1), 22-27

The relationship between the electrical and physical properties of thick film resistors was studied. The results showed that the electrical properties of the thick film resistors were affected by both the softening point and the flow point of the glass. The resistance value varied inversely with the viscosity of the glass in the case of the resistor fired at the same temperature.

Application of Copper Conductor and Ruthenium Containing Oxide-Glass Resistor to High-Frequency Hybrid IC's for a Portable Cellular Radio

T. OGAWA, M. FUJII, T. ASAI, A. IKEGAMI and T. KOBAYASHI, *IEEE Trans. Components, Hybrids, Manuf. Technol.*, 1988, **11**, (2), 211-217

The assessment of a Cu-conductor and a RuO_2 -glass resistor system and its performance in a high frequency circuit for a portable cellular radio is presented. The resistance of the Cu-compatible resistor increased after refiring at over 600°C and drastically increased as the firing temperature was raised. The results showed that the resistance change is caused by the diffusion of Ru to the Cu conductor.