

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Photoemission of Adsorbed Xenon on Pt_xNi_{1-x} (111) Single Crystal Alloy Surfaces

D. FARGUES, J. J. EHRHARDT, M. ABON and J. C. BERTOLINI, *Surf. Sci.*, 1988, **194**, (1/2), 149-158

The photoemission of adsorbed xenon and work function measurements were performed on three f.c.c.(111) oriented, Pt-Ni single crystal alloys showing a strong Pt surface segregation. For Pt-rich alloys, the first layer was a quasi-homogeneous layer, but different from a purer Pt(111) surface.

Formation of Platinum Silicide on Hydrogenated Amorphous Silicon

W. BEYER, C. E. GATTS, J. HERION, W. LOSCH and H. WAGNER, *J. Non-Cryst. Solids*, 1987, **97 & 98**, (11), 951-954

The formation of Pt silicide at the interface between a-Si:H and a surface Pt layer was found to strongly depend on the H_2 content and the structure of the amorphous films. The formation process is diffusion-limited with a diffusion coefficient comparable to c-Si for H_2 -poor a-Si:H films and also for films with microstructural defects. A considerably smaller diffusion coefficient is observed for device-grade a-Si:H films, and is attributed to H_2 accumulation at the silicide-Pt interface.

Electronic and Magnetic Properties of Uranium-Platinum Intermetallic Compounds

J. J. M. FRANSE, A. A. MENOVSKY, A. DE VISSER, P. H. FRINGS and C. VETTER, *J. Magn. & Magn. Mater.*, 1987, **70**, (1-3), 351-358

A review is given of specific heat high-field magnetisation, resistivity, high-temperature susceptibility and neutron scattering studies on various U-Pt compounds. Spin-fluctuations are found to be present in the low-temperature specific heats of UPt_2 , UPt_3 and UPt_4 , but long range magnetic order is only observed for UPt . Recent results of neutron scattering experiments are discussed. (18 Refs.)

Effect of Structure Transformation on Diffusion Characteristics of Deuterium in Palladium-Copper Alloys

A. S. ZETKIN, G. E. KAGAN and E. S. LEVIN, *Fiz. Met. Metallov.*, 1987, **64**, (5), 971-974

Studies of the temperature dependence of the diffusion coefficient, permeability and solubility of D_2 in an annealed and ordered Pd-57at.%Cu alloy showed that an ordered phase in Pd-57at.%Cu resulted in an increase in permeability and diffusion coefficient of D_2 , compared with disordered alloys, up to ~870K.

Formation of $FePd_3$ Superlattice in Fe-80at.%Pd Alloys with Additions of the Third Elements

T. TAKEZAWA and K. TABEBAYASHI, *J. Jpn. Inst. Met.*, 1987, **51**, (9), 791-796

X-ray diffraction, microscopic, thermoelectric power and electrical resistivity studies of the effects of additional elements in 80at.%Pd-Fe alloys on the formation of $L1_2$ type superlattices were studied. Results showed that a $FePd_3$ superlattice ($L1_2$ type) is formed at 80at.%Pd-Fe ($A1$ type) containing up to 8at.% of Mn, Al, In and Ga. The ordered domain increased with increasing concentration of Al. The thermoelectric power and the electrical resistivity of the alloys increased with the form of $FePd_3$ superlattice on ordering. The formation of $FePd_3$ superlattice in 80at.%Pd-Fe alloys was quantitatively explained by the Brillouin Zone effect.

Adsorption and Disproportionation of Carbon Monoxide on Palladium Alloys

O. S. GU'RYANOVA, YU. M. SEROV, A. L. LAPIDUS, R. V. DMITRIEV, S. G. GUL'YANOVA, V. M. GRYAZNOV and KH. M. MINACHEV, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, (11), 2428-2430

Studies of adsorption and disproportionation of CO on the clean surfaces of binary alloys Pd-10wt.%Ru and Pd-5.5wt.%Ni were made on samples subjected to oxidation-reduction treatment at 773K; and the effect of H_2 on these processes was explained. The results showed that on Pd-Ru alloys CO is adsorbed in two forms, one of which is connected with CO dissociation. In the presence of H_2 on the surface of binary Pd-Ru and Pd-Ni alloys, a decrease in the probability of CO_2 formation is observed.

FEM Study of the Pd- WO_x -W System

J. ŠVOTOLA and Z. KNOR, *Appl. Surf. Sci.*, 1988, **31**, (2), 173-178

The Pd- WO_x -W system was studied in a field emission microscope (FEM) as a model of a supported metal catalyst. The results showed that the Pd layer deposited onto an oxidised W tip is visible in the FEM. The oxide layer thus prepared is continuous but no contact of Pd with W was established.

A Low-Temperature ^{119}Sn Mössbauer Study of $ErPd_2Sn$

T. SHINJO, J. SAKURAI, K. MIBU and T. KUSUDA, *J. Phys. Soc. Jpn.*, 1987, **56**, (9), 3035-3037

Mössbauer measurements on ^{119}Sn in $ErPd_2Sn$ were carried out at a much lower temperature than the Néel temperature, at 1.0K. The transferred hyperfine field in the antiferromagnetic state is observed to be 7kOe. By applying external fields at 4.2K, the hyperfine field at the paramagnetic saturation is estimated to be 50kOe.

X-Ray Absorption Near-Edge Structure Evidence for Direct Metal-Metal Bonding and Electron Transfer in Reduced Rh/TiO₂ Catalysts

D. E. RESASCO, R. S. WEBER, S. SAKELLSON, M. McMILLAN and G. L. HALLER, *J. Phys. Chem.*, 1988, **92**, (1), 189-193

A comparison between the X-ray absorption near-edge structure (XANES) of Rh metal and the intermetallic compounds RhTi and Rh₃Ti, and the XANES of several Rh/TiO₂ catalysts, showed that the same kind of Rh-Ti bonding occurs in the intermetallic compounds as develops in the catalysts after they were reduced at >623K. The results are given as evidence for net electron transfer from reduced TiO₂ to at least some of the Rh in the supported samples.

Electronic, Lattice and Superconducting Properties of B2 Alloys V_{54-x}Ru₄₆Os_x and V₅₄Ru_{46-x}Os_x

A. OOTA, Y. DOSSMANN and R. KUENTZLER, *J. Phys. F*, 1987, **17**, (11), 2285-2293

Electronic, lattice and superconducting properties were studied using low-temperature specific heats on B2 systems V_{54-x}Ru₄₆Os_x and V₅₄Ru_{46-x}Os_x. A cubic-to-tetragonal transformation occurs upon cooling and shows a decisive correlation with superconductivity. An increase in x in V_{54-x}Ru₄₆Os_x, where the electron:atomic ratio e:a increased linearly with x, causing a rise of the transformation temperature T_L, lowered the electronic specific heat coefficient γ and the superconducting transition temperature T_c, while it had no effect on the Debye temperature.

The Constitution of the Mo-Ru System

H. KLEYKAMP, *J. Less-Common Met.*, 1988, **136**, (2), 271-275

Studies of the constitution of the Mo-Ru system at 900-2000°C showed that the system is of the eutectic type with a eutectic temperature of 1955°C and a eutectic composition of ~ 42at.%Ru. The maximum solubility of Ru in Mo is 32.4at.%Ru and of Mo in Ru is 51.5at.%Mo at 1935°C. The only intermediate phase, Mo₅Ru₃, present at 36.7-39.4at.%Ru, is formed by peritectoid reaction at 1915°C and is decomposed by a eutectoid reaction at 1143°C.

Magnetic Moments and ⁵⁷Fe Hyperfine Field Interactions in Y(Fe_{1-x}Ru_x)₂ Ternaries

Y. ANDOH, T. HASHIMOTO, H. FUJII, T. OKAMOTO and H. FUJIWARA, *J. Magn. & Magn. Mater.*, 1987, **70**, (1-3), 168-170

Studies of magnetisation and of ⁵⁷Fe Mössbauer spectra for Y(Fe_{1-x}Ru_x)₂ were performed. The C15 type cubic structure was stabilised for x ≤ 0.6 and the C14 type hexagonal structure for x > 0.7. The C15 compound was ferromagnetic with T_c > 200K and its saturation moment decreased monotonically with increasing x, while the ⁵⁷Fe hyperfine field decreased only slightly with x.

CHEMICAL COMPOUNDS

Tl₂Pt(CN)₄: A Noncolumnar, Luminescent Form of Pt(CN)₄²⁻ Containing Pt-Tl Bonds

J. K. NAGLE, A. L. BALCH and M. M. OLMSTEAD, *J. Am. Chem. Soc.*, 1988, **110**, (1), 319-321

The novel structure of colourless crystals Tl₂Pt(CN)₄ is reported. The structure is non-columnar, but exhibits covalent Pt-Tl bonding. The crystals show an intense blue luminescence at 22,500 cm⁻¹ at 298K when irradiated in the near u.v.

Solid Phase Thermal Conversion of Binary Palladium(II) Complex Compounds and Transition Metals of the Type [M(en)₃][Pd(NCS)₄]

L. YA. PYZHOVA and E. N. KALYUKOVA, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1987, **30**, (12), 134-136

Thermogravimetric and spectroscopic studies were carried out on the behaviours of bimetallic complex compounds of the type [M(en)₃][Pd(NCS)₄] (where M = Ni, Zn, Cd, Cu) during thermal treatment. The results showed that during fusion, the intramolecular rebuilding of complexes occurred, on which a formation of polymeric compounds was superimposed at the expense of intermolecular interactions of thiocyanate and ethylenediamine ligands.

ELECTROCHEMISTRY

Metallocomplex Catalysis in Electrode Processes

O. N. EFIMOV and V. V. STRELETS, *Usp. Khim.*, 1988, **57**, (2), 228-253

A review is given of the application of metallo-complexes, including platinum group metals, as accelerators of electrode processes. General principles of the construction of metallo-organic electrocatalytic systems are analysed. The results of studies carried out during the last 10 years are presented. (177 Refs.)

Electrochemical Pretreatment of Thin Film Platinum Electrodes

M. JOSOWICZ, J. JANATA and M. LEVY, *J. Electrochem. Soc.*, 1988, **135**, (1), 112-115

Thin film noble metal electrodes and electrode-arrays prepared by a photolithographic process suffer from surface contamination by traces of transition metals and oxides used as adhesion promoters at the insulating substrates. A simple electrochemical pretreatment was developed which removes these contaminants from the surface. It consists of electrochemical etching of the surface by pulsing it at 0 to +2V in a solution of 0.08M EDTA, 5.2% NH₄OH and 2.7 × 10⁻⁴M H₂O₂ for 5-10 min. It is followed by cycling of the applied potential at 0.4 to -0.4V in 1M KNO₃ for 10 min.

Radiotracer Study of the Adsorption of 2-Naphthoic Acid at a Platinized Platinum Electrode

G. HORANYI and E. M. RIZMAYER, *Electrochim. Acta*, 1988, **33**, (1), 113-116

Studies of the adsorption of 2-naphthoic acid on a platinized Pt electrode made by a radiotracer method in both acid and alkaline media showed irreversible strong chemisorption. The elimination of chemisorbed species was achieved by reduction and oxidation. The behaviour of chemisorbed species during cyclic voltammetric measurements was studied. It was shown that adsorption of 2-naphthoic acid exerts a significant effect on the specific adsorption of anions.

Influence of Electrolyte Acidity on the Nucleation Kinetics of Silver and Mercury on Platinum

E. MICHAILOVA, V. TSAKOVA and A. MILCHEV, *Bulgar. Akad. Nauk, Izv. Khim.*, 1987, **20**, (4), 537-541

The electrochemical nucleation of Ag and Hg on Pt was studied in electrolytes with acidities of pH=0.9-2.5 for Ag and pH=1.2-2.0 for Hg electrodepositions. A marked pH dependence of the stationary nucleation rate and the induction time was observed. This effect is related to changes in the state of the oxidised Pt substrate. The possibility of using the process of nucleus formation as a sensitive indicator of the state of the electrode surface is discussed.

Adsorption of Nitrocompounds on Platinum, Deposited on Platinum, Titanium and Titanium Dioxide

T. M. GRISHINA and O. K. LEBEDEVA, *Vestn. Mosk. Univ., Ser. Khim.*, 1988, **29**, (1), 66-69

The effect of structure of the electrode-catalyst on the nature of organic materials and its adsorption characteristics was studied on samples, prepared by electro-deposition of Pt on Pt, Ti and TiO₂, at a current of 6mA/cm² from H₂PtCl₆ followed by preliminary treatment in 1NH₂SO₄, during adsorption of nitroethane and nitrobenzene. The freshly prepared and stabilised Pt/TiO₂ cathodes showed similar catalytic properties to those obtained on platinised Pt.

Methanol Oxidation on Unsupported and Carbon Supported Pt + Ru Anodes

J. B. GOODENOUGH, A. HAMNETT, B. J. KENNEDY, R. MANOHARAN and S. A. WEEKS, *J. Electroanal. Chem. Interfacial Electrochem.*, 1988, **240**, (1/2), 133-145

A novel Pt + Ru electrode material was found to be highly active for the direct electro-oxidation of methanol in H₂SO₄ solution and showed very little tendency to poisoning. X-ray photoelectron spectroscopy studies showed that the Ru is oxidised and that there is an important surface concentration of oxidised Pt. After prolonged use as a methanol-oxidation anode, the concentration of oxidised Pt was somehow increased, and there was no evidence for any Pt-CO or Pt=CO species. The data indicate that Ru is acting as a promoter of active surface oxygen.

Electrocatalysis of Oxidation of Formic Acid and Methanol by Amorphous and Crystalline Pd_{84.5}Si_{15.5} Alloys

N. S. KOPYLOVA, O. A. PETRII, YU. V. EFIMOV and L. I. VORONOVA, *Vestn. Mosk. Univ., Ser. Khim.*, 1988, **29**, (1), 99-100

Studies of the processes of electro-oxidation of formic acid and methanol on amorphous and crystalline Pd_{84.5}Si_{15.5} were made on amorphous alloys, prepared by quenching from the liquid state, and on crystalline PdSi alloy, obtained by annealing of rapidly quenched alloys. The catalytic activity of electro-oxidation of formic acid was as follows: PdSi > crystalline Pd > crystalline PdSi alloys. The current density during electro-oxidation of methanol on Pd and PdSi alloys was approximately less, by an order, than during electro-oxidation of formic acid.

Chemisorption and Electroreduction of Acetone on the Powder Rhodium-Nickel Catalysts

A. D. SEMIONOVA and I. A. BARDINA, *Vestn. Mosk. Univ., Ser. Khim.*, 1987, **28**, (5), 456-459

Studies of the catalytic activity of Rh, Ni and Rh-Ni containing 75, 60, 50 and 25 at.%Rh were performed during acetone electroreduction in 1N KOH. The results showed that the most active were 25at.%Rh-Ni catalysts with a specific rate of electroreduction 3-4 times higher than pure Rh and 6 times higher than Ni, during all the studied potentials. The increased activity of Rh-Ni catalysts during electroreduction of acetone can be varied by composition of the catalysts, and also by changing the adsorption condition of the organic materials.

The Electrochemical Reduction of Aqueous Carbon Monoxide and Methanol to Methane at Ruthenium Electrodes

D. P. SUMMERS and K. W. FRESE, *J. Electrochem. Soc.*, 1988, **135**, (1), 264-265

The electrochemical reduction of aqueous CO and CH₃OH to CH₄ at electroplated Ru metal electrodes showed that Ru electrodes can reduce both CO and CH₃OH to CH₄ under conditions similar to those for the reduction of CO₂ to CH₄. Electrolysis of CO was conducted under 1atm CO, and CH₃OH was electrolysed under a N₂ atmosphere. The rate of reduction of CH₃OH to CH₄ increased with temperature.

Ruthenium Dioxide as a Hydrogen-Evolving Cathode

E. R. KÖTZ and S. STUCKI, *J. Appl. Electrochem.*, 1987, **17**, (6), 1190-1197

RuO₂ was investigated as a cathode material for H₂ evolution in 1NH₂SO₄. A Tafel slope of 40mV was obtained and an exchange current density of 6.10⁻⁵ A/cm², about one order of magnitude lower than for Pt, was found. Only partial reduction of the oxide occurred during H₂ evolution, perhaps as a result of H₂ penetration. RuO₂ cathodes are almost insensitive to poisoning by metal ions in solution. The stability of the RuO₂ cathode lasted for >4000h.

On the Electrocatalytic Properties of Ruthenates

J. A. R. VAN VEEN, J. M. VAN DER EIJK, R. DE RUITER and S. HUIZINGA, *Electrochim. Acta*, 1988, **33**, (1), 51-57

The activity of non-stoichiometric Pb and Bi ruthenates, which have the pyrochlore or a related structure, in the electro-oxidation of olefins is shown to be associated with the presence of a Ru(V) surface state, which is capable of being oxidised to Ru(VI) at higher potentials. Alkanes were oxidised by Ru(VI), which was continually regenerated if the potential was kept high enough (heterogeneous redox catalysis). The availability of the Ru(V)/Ru(VI) surface couple does not only occur in the pyrochlore materials but in other materials.

PHOTOCONVERSION

Regioselective Isotopic Exchange between Propane and Deuterium over Illuminated Pt/TiO₂ Catalyst below Room Temperature

J.-M. HERRMANN, H. COURBON and P. PICHAT, *J. Catal.*, 1987, **108**, (2), 426-432

Propane-deuterium isotopic exchange over an illuminated (300-410 nm) 0.5wt.%Pt/TiO₂ (anatase) catalyst was carried out at 263K with a C₃H₈:D₂ ratio of 1:15. An initial selectivity of 100% in mono-deuteropropane was found with a non-optimised quantum yield of ~ 0.01. The photocatalytic mechanism was based on the activation of the deuteroyl OD⁻ groups of titania, which are neutralised by the photoproduct holes and subsequently react with weakly adsorbed propane molecules, thus exchanging one H atom per period of adsorption. Long-duration tests indicated that the secondary H atoms exhibit a much slower exchange rate which induces the regioselectivity.

Effective Photoreduction of CO₂/HCO₃⁻ to Formate Using Visible Light

D. MANDLER and I. WILLNER, *J. Am. Chem. Soc.*, 1987, **109**, (25), 7884-7885

The design of a novel heterogeneous Pd colloid stabilised by β -cyclodextrin and its application in reducing CO₂/HCO₃⁻ to formate by the use of MV⁺ and visible light is reported. High quantum yields of H are reported for the formate production. The β -cyclodextrin support strongly affects the catalyst activity. The catalyst does 10 turnovers.

Luminescent Alkyl Complexes of Iridium

P. BRADLEY, C. E. JOHNSON and R. EISENBERG, *J. Chem. Soc., Chem. Commun.*, 1988, (4), 255-257

A series of luminescent alkyl complexes of formula IrR(CO)L₂(mnt), where mnt = maleonitriledithiolate, R = Me, Et, Pr and CH₂CN, and L is a triarylphosphine, were characterised. Photolysis of IrMe(CO)(PPh₃)₂(mnt) showed that Ir-Me bond homolysis was favoured to CO photodissociation.

Efficiency of Charge Separation in the Vesicular System: Ru(bpy)₃²⁺ (Inside)-Viologen (Membrane)-Oxidant (Outside)

N. K. KHANNANOV, V. A. KUZMIN, P. P. LEVIN, V. YA. SHAFIROVICH and E. E. YABLONSKAYA, *New J. Chem.*, 1987, **11**, (10), 687-691

The electron transfer across the vesicular wall was studied by flash and laser photolyses for the title system. Ru(bpy)₃²⁺ (inner solution) is dynamically quenched by viologen (bilayer). Trans-membrane transfer of the electrons is controlled by the viologen radical diffusion across the bilayer and depends on the temperature and phase state of the membrane. The efficiency of charge separation (η) is determined by the competition between the trans-membrane transfer of the electrons and recombination of Ru(bpy)₃³⁺ and the radical ($\eta = 0.1-0.2$ under optimum conditions).

ELECTRODEPOSITION AND SURFACE COATINGS

The Effect of a High Voltage Corona-Discharge on Electroactive Pt-Polymer Composites

W. B. JOHNSON, *J. Electrochem. Soc.*, 1987, **134**, (11), 2802-2804

A mixture of Pt powder of particle size 0.2-1.2 μ m, a phenoxy resin and toluene were made into a composite, and applied to cold-rolled steel panels. Samples were treated with a corona discharge by passing the coated panel through a 2kW 0-9.6kHz voltage field with energy input of about 2J/cm² to the surface. Discs were then punched and examined in a standard 3 electrode cell and SEM micrographs were made. The peaks associated with H₂ adsorption and evolution and Pt oxidation were examined, and the currents were approximately 4 times higher than for a pure Pt surface of the same nominal area. The coatings behave like pure Pt, except for a 4-fold increase in effective surface area. Different coating thicknesses were investigated.

Oxide Adhesion and Growth Characteristics in Platinum-Modified Aluminide Coatings

M. S. FARRELL, D. H. BOONE and R. STREIFF, *Surf. Coat. Technol.*, 1987, **32**, 69-84

The improved lifetime of Pt-modified aluminide coatings under high temperature conditions, hot corrosion and cyclic oxidation was attributed mainly to the excellent oxide adherence exhibited by these systems. In this study the effects of pre-aluminising surface smoothness and coating structure, for both Pt-modified and unmodified aluminide coatings on a typical nickel-based superalloy (IN-738), were examined in a cyclic oxidation environment at 1100°C. Weight change measurements were used to determine the coating scale adherence characteristics and to quantify the cyclic oxidation behaviour effect of the various coating structures.

Structure and Hot Corrosion Behaviour of Platinum-Modified Aluminide Coatings

R. STREIFF, O. CERCLIER and D. H. BOONE, *Surf. Coat. Technol.*, 1987, 32, 111-126

The well-known differences in performance of Pt-modified aluminide coatings were studied in terms of their unique structural and diffusional features. Changes in the Pt and substrate element concentration and in the NiAl phase matrix lattice parameter suggested that one important function of the Pt is for the rapid self-healing of the formed oxide scale due to Al diffusion to the surface. Results of these analyses are discussed in terms of exposition test data and theories.

The Fretting of Electrodeposited Contact Coatings

J. W. SOUTER and W. STAUNTON, *Trans. Inst. Met. Finish.*, 1988, 66, (1), 8-14

A brief summary is given of the published work relating to an electrical contact phenomena known as fretting wear or fretting corrosion, including examples of a failure in gold plated contacts, together with the results of laboratory fretting wear tests on electroplated coatings which include Pd, Pd-Ni, Au and Sn. It is shown that differences exist between deposits of metals or alloys obtained from different proprietary solutions.

APPARATUS AND TECHNIQUE

Enzyme Microsensor for Glucose with an Electrochemically Synthesized Enzyme-Polyaniline Film

H. SHINOHARA, T. CHIBA and M. AIZAWA, *Sens. Actuators*, 1988, 13, (1), 79-86

An enzyme microsensor for glucose was made by the electrochemical polymerisation method. A glucose oxidase-entrapped polyaniline (GOD-polyaniline) film was deposited on the top of a Pt fibre (50 μ m in diameter) by the electrochemical oxidative polymerisation of aniline in a pH 7 buffer solution, in the presence of glucose oxidase. Glucose was amperometrically measured with the electrochemically fabricated microsensor in the concentration range 10^{-4} to 5×10^{-3} M.

Design of Platinum Hot Wire Gas Sensors

W. M. SEARS and S. R. MORRISON, *Sens. Actuators*, 1988, 13, (2), 89-101

The design characteristics of low-power Pt gas sensors were studied. A prototype sensor design is given which uses a small piece of Pt ribbon welded to a ceramic header with a wire mesh cathode to collect the positive ions. The ionic current is measured by a battery-run picoammeter circuit biased to float at -120V. At the operating temperature of 800°C the power consumption is ~2W. The prototype is capable of detecting iso-octane vapour down to a concentration of 2ppm. The sensor is selective for long-chain hydrocarbons.

Integrated Hydrogen Leak Detector with a Tunnel MIS Structure

K. MURAKAMI, D.-B. YE and T. YAMAMOTO, *Sens. Actuators*, 1988, 13, (4), 315-321

A simple integrated H leak detector was constructed which consisted of a Pd-Si tunnel MIS diode for the H sensor, a diffused resistor layer for the inside heater and a p-n junction diode for temperature control. Measurements were made on the response characteristics to H at different device temperatures and H concentrations. The results show that the newly constructed detector can be used as a practical detector for small leakages of H at a device temperature of 100-120°C. It is shown that the tunnel MIS diode with a hole-structure Pd layer drastically improves the H sensitivity.

Use of Ir₄(CO)₁₁ to Measure the Lengths of Organic Molecules with a Scanning Transmission Electron Microscope

F. R. FURUYA, L. L. MILLER, J. F. HAINFELD, W. C. CHRISTOPFEL and P. W. KENNY, *J. Am. Chem. Soc.*, 1988, 110, (2), 641-643

A long, rigid organic spacer with specifically attached Ir₄(CO)₁₁ labels was successfully tested for use as a metal-cluster label for accurately measuring molecular distances by scanning transmission electron microscopy. Cluster labelling is now expected to be developed for measuring the length of molecular lines on a surface.

Thick-Film Voltammetric Sensors Based on Ruthenium Dioxide

M. LAMBRECHTS, W. SANSEN, J. SULS and S. PASZCZYNSKI, *Sens. Actuators*, 1988, 13, (3), 287-292

The electrochemical properties of films made of different resistive pastes based on RuO₂, Bi₂Ru₂O₇ or Au and applied to a Al₂O₃ substrate by planar thick-film technology were studied in voltammetric experiments. Results indicate that thick-film RuO₂ electrodes give considerable advantages over classically manufactured electrodes. The preparation of these electrodes is straightforward and easy. They behave well with redox systems, have small capacitive currents and are robust.

JOINING

Formation of Coloured Area on the Surface of Platinum Alloys during Welding

V. A. YASTREBOV, D. S. TYKCHINSKII, E. I. RYTVIN and N. A. TRUSOVA, *Svar. Proizvod.*, 1987, (2), 41-42

Studies were carried out on samples of commercial Pt alloys in order to explain the mechanism of the formation of coloured areas located ~3-5mm from the point, during the microplasma, Ar-arc and gas welding of the Pt alloys. The formation of coloured zones was found to be due to the dissociation of PtO₂, RhO₃ and IrO₃ during welding. The coloured area has no effect on the performance of the welded parts and totally disappeared at >1000-1100°C.

HETEROGENEOUS CATALYSIS

Metallocarbonyl Catalytic Production of Organic Compounds from CO and H₂

A. L. LAPIDUS and M. M. SAVEL'EV, *Usp. Khim.*, 1988, 57, (1), 29-49

A review is given of preparation of organic compounds from CO and H₂ on catalysts, including platinum group metal catalysts, obtained by thermal decomposition of metal carbonyls on inorganic substrates. Special features of the interaction of various carbonyl metals with substrates and the mechanism of formation of metallocarbonyl catalysts are considered. (165 Refs.)

Kinetics of Decomposition of HCHO, HCOOH, CH₃OH and N₂H₄ on Pt and Rh Surfaces

G. A. PAPAPOLYMEROU and L. D. SCHMIDT, *Langmuir*, 1987, 3, (6), 1098-1102

The decomposition kinetics of the title compounds on polycrystalline Pt and Rh wires were studied in a differential flow reactor for reactant pressures between 0.02-1 torr and at 400-800K. Below 800K rates of N and CH₄ formation are comparable, with N predominant at >800K. All rates of formation fit quantitatively with simple Langmuir-Hinshelwood intermolecular rate expressions with an accuracy of ~ 30%. Above 800K, all rates become temperature dependent and are identical to within a factor of ~ 3. Rates of all the reactions are also identical to ~ a factor of 2 on Pt and Rh, although the rate parameters were slightly different.

Reforming of C₇ Hydrocarbons on a Sulfided Commercial Pt/Al₂O₃ Catalyst

P. A. VAN TRIMPONT, G. B. MARIN and G. F. FROMENT, *Ind. Eng. Chem. Res.*, 1988, 27, (1), 51-57

The kinetics of the reforming of C₇ hydrocarbons were studied in a tubular reactor on a sulphided commercial Pt/Al₂O₃ catalyst under both deactivating and non-deactivating conditions at 582-763K, total pressure of 3-21 bar and H₂ partial pressure of 2-20 bar. Electrobalance experiments showed that the isomerisation rate, the dehydrogenation rate and the coking rate exponentially decreased with coking.

Performance of Pt/Al₂O₃ Catalysts in Automobile Engine Exhaust with Oscillatory Air/Fuel Ratio

B. K. CHO, *Ind. Eng. Chem. Res.*, 1988, 27, (1), 30-36

Performance of Pt/Al₂O₃ catalysts for the removal of CO, NO and hydrocarbons in engine exhaust was studied using a fixed-bed reactor connected to a dynamometer-mounted engine. The effect of air: fuel ratio oscillation on the catalyst performance was studied over a wide temperature range. Results showed good activity of fresh Pt/Al₂O₃ catalysts for the oxidation of CO and hydrocarbons as well as for the reduction of NO, when the feed composition oscillated symmetrically around a time-averaged stoichiometric point.

Effect of Hydrogen on the Selectivity of Pt-Containing Pentasil Catalysts in n-Hexane Transformations

O. V. BRAGIN, T. V. VASINA, E. G. HELKOVSKAYA-SERGEEVA, M. A. DOBROVOLSZKY and Z. PAÁL, *J. Catal.*, 1988, 109, (1), 156-162

Transformations of n-hexane were studied over ZSM-5-type Na-, H-, and Pt/H- pentasils with SiO₂: Al₂O₃ = 35; Pt = 0.5%, in flow and pulse systems in the presence of H₂ and N₂. The Na-form was almost inactive, the H-form had acidic properties with hardly any H effect. Aromatisation and isomerisation were enhanced over the Pt/H- zeolite, the former being bifunctional, while the isomerisations are metal-catalysed reactions.

Optimum Chlorine Content on a Commercially Operated Pt-Re/Al₂O₃-Cl Catalyst as a Function of the Specific Surface Area

J. M. GRAU, E. L. JABLONSKI, C. L. PIECK, R. J. VERDERONE and J. M. PARERA, *Appl. Catal.*, 1988, 36, (1-2), 109-117

Changes in the activity, selectivity and stability of fresh and industrially regenerated Pt-Re/Al₂O₃-Cl catalysts with different numbers of operation cycles, due to changes in the Cl content, were studied. Similar variations in activity and selectivity as a function of the Cl⁻ content occurred for all the catalysts studied.

Catalyst Dehydrogenation of Cyclohexene on Silica Overlayer Films

J. M. COGEN, K. EZAZ-NIKPAY, R. H. FLEMING, S. M. BAUMANN and W. F. MAIER, *Angew. Chem., Int. Ed. Engl.*, 1987, 26, (11), 1182-1184

Studies were made of the catalytic dehydrogenation of cyclohexene on SiO₂/Pt/Si overlayer films in the presence of H₂ in order to find a noble metal catalyst which could be resistant to poisoning. The above reaction yielded benzene and cyclohexane. The same result occurred over Pt/Si, except that the activity of this reaction was lower by a factor of 100. A SiO₂ overlayer of 0 to 30nm thickness lowered the activity exponentially, after which the value remained constant up to 2200 nm. The results showed that instead of the transition-metal surface, "active hydrogen" (atomic H) is the real catalytic specie.

Kinetics of Hydrogenation of Alkynes and Dienes on Palladium Catalyst

L. ČERVENÝ and S. ŘEHŮRKOVÁ, *Collect. Czech. Chem. Commun.*, 1987, 52, (12), 2909-2917

Alkyne and diene substrates (C₆-C₁₀) in hexane and methanol were hydrogenated over a 3%Pd/activated C at 20°C and atmospheric pressure. The selectivities in the competitive hydrogenation of substrate pairs were established, and the relative adsorption coefficients of the substrates were calculated from them. The effect of substrate structure and the solvent effect on the hydrogenation rate and relative adsorption are discussed for the alkyne and dienic substrates studied.

Pd-Based Diffusion Membranes as Ethylene Hydrogenation Catalysts

I. T. CAGA, J. M. WINTERBOTTOM and I. R. HARRIS, *Inorg. Chim. Acta*, 1987, **140**, (1-2), 53-55

Studies were made on two Pd rich membranes Pd-23at.%Ag and Pd-7.8at.%Y, in order to find a Pd-based alloy with permeability to H₂ and good mechanical properties. The catalytic activities of the membranes were studied during hydrogenation of ethylene. The permeabilities of the Pd-7.8at.%Y membrane were greatly in excess of those of the Pd-23at.%Ag membrane and at 300°C and 6.8 bars of differential pressure the permeability of the Pd-7.8at.%Y was higher by 3.65 times.

Effect of Preliminary Treatment of Rhodium Wire on the Activity and Selectivity in Propane Hydrogenolysis

V. M. GRYAZNOV, E. V. SKAKUNOVA and M. M. ERMILOVA, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, (11), 2440-2442

The effect of tempering on the activity and selectivity of Rh wire was studied during propane hydrogenolysis at atmospheric pressure and 473-573K. High temperature annealing of the Rh wire catalyst followed by quick cooling increased the rate of the hydrogenolysis reaction and also the selectivity towards CH₄, as compared to slow cooling when the selectivity is towards C₂H₆. Annealing and cooling in air increased the catalyst activity at 573K by 1.6 fold compared to annealing in inert gas.

Hydrogenation and Hydroformylation with Supported Rhodium Catalysts. Effect of Adsorbed Sulfur

Y. KONISHI, M. ICHIKAWA and W. M. H. SACTLER, *J. Phys. Chem.*, 1987, **91**, (24), 6286-6291

The effects of increasing S coverage on Rh surfaces during ethylene hydroformylation and hydrogenation, on freshly reduced Rh/SiO₂ samples, exposed to a flow of H₂ containing 10.9ppm of H₂S, were studied for CO chemisorption, its i.r. spectrum and catalytic activity. The adsorbed S selectively inhibited the chemisorption of bridging CO.

Structure and Catalytic Activity of Supported Metal Complexes. 2. Synthesis of Rhodium Complexes Supported on Silica Gel Modified by Phosphorus- and Nitrogen-Containing Ligands

V. F. DOVGANYUK, L. I. LAFER, V. I. ISAEVA, ZH. L. DYKH, V. I. YAKERSOV and V. Z. SHARF, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, (12), 2660-2665

Rh complexes supported on SiO₂ gel, and modified by P- and N-containing ligands, were prepared by modification of silicates by aluminophosphine groups and by Rh complexes RhCl(cyd)₂, RhCl(PPh₃) and RhCl₃ (cyd=cyclooctadiene-1,5) immobilised on them. Spectroscopic studies showed the formation of aluminophosphine groups on the silicate surface during interaction of γ -aminopropyl-containing silicates and Ph₂PCl.

Selectivity Change in CO Hydrogenation by Oxidation-Reduction Treatment of Ru/Al₂O₃: Selectivity versus Morphology of Ru

Z.-Z. LIN, T. OKUHARA and M. MISONO, *J. Phys. Chem.*, 1988, **92**, (3), 723-729

The effects of oxidation-reduction treatment on the microstructure of Ru particles and the catalytic activity and selectivity of Ru/Al₂O₃ for CO hydrogenation were studied. The Ru/Al₂O₃ catalysts were prepared from Ru₃(CO)₁₂, which consisted of small particles (10Å), and from RuCl₃, which consisted of aggregates of small particles, respectively. Oxidation with O₂ at 500°C and subsequent reduction changed the Ru particles to large single crystallites. In CO hydrogenation, the main yield after only reduction was higher hydrocarbons, but the catalysts pretreated with O₂ produced mainly methane. The results showed that the significant change in the selectivity is due to changes in microstructure of the Ru particles.

Electrophoretic Study of RuO₂/ γ -Al₂O₃ Samples Used in the Water Gas Shift

S. A. MOYA, A. MANSILLA and F. J. GIL LLAMBIAS, *Bull. Soc. Chim. Belg.*, 1988, **97**, (1), 9-15

The RuCl₃, supported on γ -Al₂O₃ and calcinated in air at 500°C generated an active catalytic phase RuO₂/ γ -Al₂O₃ for the water-gas-shift-reaction, at 100-140°C and atmospheric pressure. Both the apparent surface coverage of Al₂O₃ by RuCl₃, as measured by electrophoresis, and the activity occurred simultaneously with metal deposited on the samples.

The Fischer-Tropsch Synthesis over a Ruthenium Catalyst under Composition Cycling

G. S. ROSS, R. R. HUDGINS and P. L. SILVESTON, *Can. J. Chem. Eng.*, 1987, **65**, (6), 958-965

The effect of feed composition cycling on the activity and selectivity of the Fischer-Tropsch synthesis over a 0.5%Ru/Al₂O₃ catalyst was studied using a fixed-bed reactor at 211°C and 446kPa total pressure. Forced composition cycling suppressed the overall synthesis rate but increased the rates of formation of the C₁ to C₄ paraffins and shifted the paraffin:olefin ratio.

Characterisation of Supported Ruthenium Catalysts by Thermal Analysis

LIU JINXIANG, YANG LIXIN, GAO SHIUYING, HU LIJUAN, TANG RENYUAN and LIANG DONGBAI, *Thermochim. Acta*, 1988, **123**, 121-133

The reduction-oxidation behaviour of unsupported and supported Ru components was studied, and the extent of metal-support interaction was characterised. The sintering stability of the Ru crystallites on Al₂O₃ and SiO₂ supports was studied through reduction-oxidation cycles by DTA and the effect of chloride impurities on the reduction-oxidation behaviour was also examined. Reduction kinetics parameters were determined by the Freeman-Carroll procedure.

Selective Acceleration Effects of K-Addition in Hydrogenolysis of Cyclohexane over Ruthenium Supported on Silica

Z.-Z. LIN, T. OKUHARA and M. MISONO, *Chem. Lett. Jpn.*, 1987, (11), 2201-2202

Studies of the effects of K addition to a 2.5wt.%Ru/SiO₂ catalyst were made during cyclohexane hydrogenolysis and dehydrogenation in a flow system under 1 atm. A mixture of H₂ and cyclohexane (H₂ : cyclohexane = 5) was supplied at 300°C. During hydrogenolysis of cyclohexane the activity of Ru-K/SiO₂ with a K : (K+Ru) ratio of 0.2 was higher than that of Ru/SiO₂, yielding mainly methane. As the K content (K : (Ru + K)) increased from 0.2, the activity decreased.

HOMOGENEOUS CATALYSIS

Hydrosilylation of Unsaturated Compounds in the Presence of Thiocarbamide Platinum(II) and Palladium(II) Complexes

V. Z. BROVKO, N. V. VOROB'EV-DESYATOVSKII and YU. N. KUKUSHKIN, *Zh. Prikl. Khim. (Leningrad)*, 1987, 60, (11), 2554-2556

Hydrosilylation of 1-heptene and phenylacetylene by methylchlorosilane was performed in the presence of Pt(II) and Pd(II) complex catalysts of a cationic type, containing thiocarbamide and their substituted derivatives, at 180-220°C. The results showed that Pt(II) thiocarbamide complexes of the cationic type were highly selective during the studied reaction.

Charge Reversal of Electrophilic π -Allylpalladium Intermediates; Carbonyl Allylation by Allylic Acetates with PdCl₂(PhCN)₂-SnCl₂

Y. MASUYAMA, R. HAYASHI, K. OTAKE and Y. KURUSU, *J. Chem. Soc., Chem. Commun.*, 1988, (1), 44-45

The PdCl₂(PhCN)₂-SnCl₂ system in 1,3-dimethylimidazolidin-2-one (DMI)³ was found to promote carbonyl allylation by an apparent charge reversal of π -allylpalladium intermediates which occurred without homocoupling. The allylation of an aldehyde was chemoselectively performed in the presence of a ketone group or an ester group.

Catalysis of Cyclopropenyldiene Palladium(II) Complexes for the Isomerization of Quadricyclane to Norbornadiene

S. MIKI, T. OHNO, H. IWASAKI, Y. MAEDA and Z.-I. YOSHIDA, *Tetrahedron*, 1988, 44, (1), 55-60

New Pd complexes of cyclopropenyldienes of the type trans-Cl₂Pd(CP)(Py-X) were prepared, where CP is di-*t*-butylcyclopropenyldiene or bis(diisopropylamino)cyclopropenyldiene and Py-X is 4-substituted pyridine (X = H, CH₃, CN). The complex showed high catalytic activity towards the cyclo-reversion of quadricyclane to norbornadiene.

Palladium-Catalysed Reaction of Propargylic Acetates with Carbonyl Compounds by SmI₂

T. TABUCHI, J. INANAGA and M. YAMAGUCHI, *Chem. Lett. Jpn.*, 1987, (11), 2275-2278

Reductive addition of propargylic acetates to carbonyl compounds proceeded smoothly at room temperature in the presence of a catalytic amount of Pd(PPh₃)₄ and SmI₂ to yield the corresponding acetylenic and/or allenic alcohols with appreciable selectivity.

Kinetics and Mechanism of Oxidation of Propylene to Allylacetate in Palladium Clusters Solutions

I. P. STOLYAROV, M. N. VARGAFIJK and I. I. MOISEEV, *Akad. Nauk SSSR, Kinet. Katal.*, 1987, 28, (6), 1359-1363

The kinetics and mechanism of the oxidation of propylene to allylacetate in cluster solutions of Pd₅₆₁Phen₆₀(OAc)₁₈₀ and Pd₅₆₁Phen₆₀(PF₆)₆₀ were studied by gas-liquid chromatography at 40-90°C. The rate of reaction was found to be in proportion to the concentrations of propylene and clusters in solution. At higher partial O₂ pressure, the reaction was inhibited by O. The reactive mechanism is given.

Catalytic and Structural Properties of Iridium-Iridium Dioxide Colloids

A. HARRIMAN, J. M. THOMAS and G. R. MILLWARD, *New J. Chem.*, 1987, 11, (11/12), 757-762

Colloids of Ir and IrO₂.xH₂O were prepared by hydrolysis and reduction of hexachloroiridates, and were characterised by microscopic X-ray diffraction, spectroscopic, cyclic voltammetry and electrophoresis techniques. Colloids of Ir are crystalline, but those of IrO₂.xH₂O are amorphous and slowly aggregate, even when protected with a surface layer of polymer. Colloidal Ir was a good catalyst for reduction of H₂O to H₂, hydrogenation of unsaturated groups and dissociations of formic acid and hydrogen peroxide. Colloids of IrO₂.xH₂O catalysed the oxidation of H₂O to O₂, but the efficiency was only modest.

Molecular Chemistry of Bimetallic Clusters on the Basic γ -Al₂O₃ Surface: Synthesis, Reactivity, and Catalytic Activity of [H₃RuOs₃(CO)₁₂]⁻{Al} and Related Structures

J. P. SCOTT, J. R. BUDGE, A. L. RHEINGOLD and B. C. GATES, *J. Am. Chem. Soc.*, 1987, 109, (25), 7736-7744

The cluster [H₃RuOs₃(CO)₁₂]⁻{Al} was synthesised, and is assumed to be the precursor of a catalyst for the isomerisation of but-1-ene to give *cis*- and *trans*-but-2-ene. The catalyst is stable for >2000 turnovers at 53-77°C. Langmuir-Hinshelwood kinetics and i.r. spectra suggest that the catalytic cycle involves coordination of the alkene to Os in the intact molecular cluster. For ethylene hydrogenation the catalyst activity increases and cluster degradation occurs.

Catalytic Formation of Biaryls from Arenes through C-H Bond Activation by $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$ under Irradiation

T. SAKAKURA, T. SODEYAMA, Y. TOKUNAGA and M. TANAKA, *Chem. Lett. Jpn.*, 1987, (11), 2211-2214

Studies of a dehydrogenative coupling of arenes catalysed by $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$, in a new application of the C-H activation, at room temperature and under irradiation by a high pressure Hg lamp showed a yield of biaryls. The regioselectivity obtained in the reaction of toluene suggested the presence of a radical intermediate.

A Novel Wacker Route Based on Ruthenium(III) Ion for Olefin Oxidation to Ketones

M. M. TAQUI KHAN and A. PRAKASH RAO, *J. Mol. Catal.*, 1988, 44, (1), 95-105

The oxidation of 1-hexene to the end ketone 2-hexanone by O_2 was catalysed by Ru(III) ion, $[\text{RuCl}_2(\text{H}_2\text{O})_4]^+$ at 35°C (ionic strength = 0.1M) in 1:1 (v/v) water-dioxane solution at pH 2.00. The reaction showed a first-order dependence on catalyst and substrate concentrations and a one-half-order dependence with respect to O_2 concentration. A mechanism involving a combination of a peroxo-metallo cycle and the Wacker oxidation route to ketone formation is proposed. The system represents the first simple monometallic and non-corrosive pathway for Wacker oxidation of olefins to ketones, and proceeds via a turnover frequency of 62 mol ketone/mol catalyst/h at 35°C.

Ruthenium(II)-BINAP Catalysed Stereoselective Homogeneous Hydrogenation of 1,3-Diketones

H. KAWANO, Y. ISHII, M. SABURI and Y. UCHIDA, *J. Chem. Soc., Chem. Commun.*, 1988, (2), 87-88

The $\text{Ru}_2\text{Cl}_4[(R)\text{-BINAP}]_2(\text{NET}_3)^3$ [BINAP = 2,2'-bis-(diphenylphosphino)-1,1'-binaphthyl] transition metal complex catalysed hydrogenation of 1,3-diketones yielding 1,3-diols with extremely high diastereo- and enantioselectivity. The present reaction introduces a novel class of stereoselective reaction using a transition metal complex as catalyst, but also gives a powerful tool for organic synthesis.

Homogeneous Rhodium Complex-Catalysed Hydroformylation and Related Reactions of Functionally Substituted Olefins

A. M. TRZECIAK and J. J. ZIÓLKOWSKI, *J. Mol. Catal.*, 1987, 43, (1), 15-20

The Rh(I) complexes, $\text{Rh}(\text{acac})\text{P}_2$, $\text{Rh}(\text{acac})(\text{CO})_2$, HRhP , and $\text{RhP}_3\text{P}'$, where $\text{P} = \text{P}(\text{OPh})_3$ and $\text{P}' = \text{P}(\text{OPh})_2(\text{OC}_6\text{H}_4)$, were applied as catalysts during hydroformylation, isomerisation and hydrogenation of allyl alcohol, methyl acrylate and vinyl acetate. All the reactions occurred at relatively mild conditions at 1 atm H_2 or $(\text{CO} + \text{H}_2)$ pressure and at 20-40°C. This demonstrated the high catalytic activity of these studied catalysts.

Promoting Effect of Acids on the Formation of Ethylene Glycol from Synthesis Gas Catalysed by the Rhodium-Tricyclohexylphosphine System

Y. OHGOMORI, S. MORI, S.-I. YOSHIDA and Y. WATANABE, *J. Mol. Catal.*, 1987, 43, (1), 127-136

Carboxylic acids, pentafluorophenol and phosphoric acid (HX) facilitate the formation of ethylene glycol from synthesis gas catalysed by the Rh-tricyclohexylphosphine (TCP) system. Complexes recovered from the resultant solutions were identified as $\text{RhX}(\text{CO})(\text{TCP})_2$ which were stable after repeated use.

BINAP-Ruthenium(II) Dicarboxylate Complexes: New, Highly Efficient Catalysts for Asymmetric Hydrogenations

T. OHTA, H. TAKAYA and R. NOYORI, *Inorg. Chem.*, 1988, 27, (3), 566-569

The BINAP-Ru(II) complexes $\text{Ru}(\text{OCOR})_2[(R)\text{-or (S)-2,2'-bis}(\text{diarylphosphino})\text{-1,1'-binaphthyl}]$, [aryl = phenyl, p-tolyl; R = CH_3 , $\text{C}(\text{CH}_3)_3$] were prepared. X-ray crystallographic studies showed that the complex has a Δ structure, in which the BINAP-containing seven-membered chelate ring is fixed in a δ conformation. These BINAP-Ru complexes are highly efficient catalysts for asymmetric hydrogenations of various enamides, α -(acylamino)acrylic acids, α,β - and β,γ -unsaturated carboxylic acids, allylic and homoallylic alcohols and amino ketones.

Homogeneous Oxidation of Cyclohexane by a Ru(III) Analogue of the Model Peroxidase System Ru(III)-EDTA-Ascorbate- H_2O_2

M. M. TAQUI KHAN and R. S. SHUKLA, *J. Mol. Catal.*, 1988, 44, (1), 73-83

The kinetics of the oxidation of cyclohexane to cyclohexanol by H_2O_2 catalysed by the Ru(III)-EDTA-ascorbate system was studied by spectrophotometric techniques at pH 1.50-2.50, 30°C, ionic strength $\mu = 0.1\text{M}$ KNO_3 in a 1:1 (v/v) mixture of 1,4-dioxane and H_2O . The rate of oxidation of cyclohexane was first order with respect to the concentrations of ascorbate, Ru(III)-EDTA and H_2O_2 , inverse first order with respect to H ion concentration, and fractional order with respect to cyclohexane. In a proposed mechanism, the function of the two-electron donor, ascorbic acid, is to reduce the metal chelate Ru(III)-EDTA to Ru(II)-EDTA.

Stereospecific Epoxidation by Air of Cholest-5-ene Derivatives Catalysed by a Ruthenium Porphyrin

J.-C. MARCHON and R. RAMASSEUL, *J. Chem. Soc., Chem. Commun.*, 1988, (4), 298-299

A Ru porphyrin catalyst was found to catalyse the epoxidation by air of several cholest-5-ene derivatives in high yield and with nearly complete β -stereospecificity. The C-3- unprotected cholesterol was unaffected, but cholesterol acetate yielded nearly pure (>99%) $5\beta,6\beta$ -epoxide.

CORROSION PROTECTION

Effect of Conditions of Electric Spark Alloying of Titanium Surface with Palladium on the Compositions of the Phases Formed and on the Corrosion Stability of Titanium

G. P. CHERNOVA, L. P. KORNIENKO, A. E. GITLEVICH, V. V. MICHAILOV, G. M. PLAVNIK, G. N. KHRUSTALEVA and N. D. TOMASHOV, *Zashch. Met.*, 1988, **24**, (1), 53-59

Studies of phase-compositions formed on Ti surfaces during electric spark alloying with Pd, and of corrosion and electrochemical behaviour of Pd-covered-Ti were performed in 10-40% H₂SO₄ at 100°C. The results showed formation of TiPd phases on Ti surfaces with higher Pd contents, and intermetallic compounds TiPd, and Ti₂Pd₃, pure Pd and also Ti oxides were observed. The TiPd phases formed during the alloying were very effective anodes with a great increase in their corrosion stability.

GLASS TECHNOLOGY

Cw Laser Action of Er³⁺ in Double Sensitized Fluoroaluminate Glass at Room Temperature

E. HEUMANN, L. LEDIG, D. EHRT, W. SEEGER, E. W. DUCZYNSKI, H. J. V. D. HEIDE and G. HUBER, *Appl. Phys. Lett.*, 1988, **52**, (4), 255-256

Cw lasing at 1.6 μm was obtained for the first time in Cr, Yb, Er:fluoroaluminate glass which was prepared by heating to 1000-1300°C in a Pt crucible and the melt was put into preheated graphite moulds. Double step pumping via Cr³⁺ and Yb³⁺ with a krypton laser yields threshold pump power 80 mW.

ELECTRICAL AND ELECTRONIC ENGINEERING

Platinum Silicide Contact to Arsenic-Doped Polycrystalline Silicon

H.-C. W. HUANG, R. COOK, D. R. CAMPBELL, P. RONSHHEIM, W. RAUSCH and B. CUNNINGHAM, *J. Appl. Phys.*, 1988, **63**, (4), 1111-1116

PtSi contact to As-doped polycrystalline Si was studied with respect to dopant redistribution, microstructure and contact resistance. Cross-sectional transmission electron microscopy showed columnar PtSi grains and a relatively flat interface between PtSi and polysilicon. The specific contact resistance (ρ_c) decreased with increasing As concentration. However, the contact resistance to As-doped polysilicon was ten times higher than contacts to similarly doped single-crystal Si. Hall-voltage measurements showed that only ~10% of the implanted As was electrically active after 880°C, 20 min furnace annealing. Rapid-thermal annealing was then used to activate implanted As, and a much lower ρ_c was obtained.

A Comparison of the Reliability of Copper and Palladium-Silver Thick-Film Crossovers

R. R. SUTHERLAND and I. B. E. VIDELO, *IEEE Trans. Components, Hybrids, Manuf. Technol.*, 1987, **CHMT-10**, (4), 676-682

The reliability of Pd-Ag crossover systems under 85°C/85% relative humidity bias stress were shown to depend primarily on the porosity of the dielectric. All of the low-porosity dielectrics tested gave consistently good reliability, while all the high-porosity dielectrics showed considerable variation in reliability.

The Pd-Zn System for Ohmic Contacts of p-Type GaP

TAN FU LEI and GUANG KAI JENG, *Solid-State Electron.*, 1988, **31**, (1), 109-113

Studies of Pd-based metallisation on p-type GaP showed that the multi-layered Pd/Zn/Pd structure and the co-evaporated Pd/Pd-Zn structure had good ohmic characteristics after heat-treatment. Specific contact resistivity ρ_c , as low as $6.9 \times 10^{-5} \Omega\text{cm}^2$ for the surface concentration of $2-3 \times 10^{17}/\text{cm}^3$ was obtained. This is the lowest ρ_c value ever obtained for the same dopant concentrations.

TEMPERATURE MEASUREMENT

The Use of the Gallium Triple Point in Platinum Resistance Thermometer Interpolation below 273.15K

R. C. KEMP, *Metrologia*, 1987, **24**, (4), 175-179

The effect of replacing the boiling point of H₂O by the triple point of Ga in several interpolation schemes for Pt resistance thermometers below 273.15K was studied. The sensitivity of the scheme for calibration errors in the Ga point is ~5 times higher than that for calibration errors in the boiling point of H₂O.

MEDICAL USES

Design of a Double-Stranded DNA Cleaving Agent with Two Polyamine Metal-Binding Arms: Ru(DIP)₂ Macroⁿ⁺; Metal-Activated Hydrolytic Cleavage of DNA

L. A. BASILE and J. K. BARTON; L. A. BASILE, A. L. RAPHAEL and J. K. BARTON, *J. Am. Chem. Soc.*, 1987, **109**, (24), 7548-7550; 7550-7551

The synthesis and application of a novel double-stranded cleaving agent Ru(DIP)₂Macroⁿ⁺ is reported, where the cleaving agent contains two polyamine segments, which in the presence of metal ions, specifically Cu, may cleave each strand of duplex DNA. The second paper reports metal ion activated cleavage of DNA by small molecules through phosphodiester hydrolysis, yielding products which may be religated enzymatically. The greatest religation occurs with ions Zn(II), Cd(II) and Pb(II).