

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Anisotropy and Magnetostriction of Pt-Fe Alloys

M. PARDAVI-HORVATH, L. I. VINOKUROVA and V. YU. IVANOV, *J. Magn. & Magn. Mater.*, 1984, **41**, (1-3), 349-351

Temperature and magnetic field dependencies of magnetisation, magnetostriction and thermal expansion were measured for ordered Pt-Fe alloys in the range 25-32at.%Fe of the transition from antiferromagnetism to ferromagnetism, through formation of clusters embedded in the antiferromagnetic matrix. Anisotropy of the critical fields were determined and the reorientation of the vector of antiferromagnetism was followed. Tetragonal distortion of the lattice accompanies the change of the effective anisotropy field.

Solubility of Protium, Deuterium, and Tritium in the α Phase of Palladium

R. LÄSSER, *Phys. Rev. B*, 1984, **29**, (8), 4765-4768

The first solubility determinations of T in bulk Pd are presented for the pressure range $0.016 \leq p \leq 1.33$ bars, temperature range 60-400°C and concentration range, x , in PdT $_x$ of 0.0015-0.02. Also the first comparative study of the pressure-composition-temperature relationship of all H isotopes in Pd at low concentrations is described.

Some Transport Properties of Palladium Films

M. A. ANGADI and S. M. SHIVAPRASAD, *J. Mater. Sci.*, 1984, **19**, (7), 2396-2400

The effect of deposition rate and substrate temperature on the electrical resistivity, TCR and thermoelectric power of Pd films of 2-25nm thickness was found to be marked. Higher rates of deposition and substrate temperatures result in larger grains and hence changes in transport properties.

Effect of Heat-Treatment on the Hydrogen Sensitivity of ZnO Thin Films Loaded with Palladium Salts

W. B. LI, H. YONEYAMA and H. TAMURA, *Mater. Chem. Phys.*, 1984, **10**, (1), 69-81

Porous ZnO thin films were impregnated with Pd salts from their aqueous solutions, heat treated and assessed for H₂ sensitivity. During impregnation of PdCl₂, a ZnCl₂.4Zn(OH)₂ phase is formed, in a surface region which retards the appearance of the H₂ sensitivities. By heating the sample at 140-200°C this phase is decomposed, but the impregnated PdCl₂ is not decomposed, and a remarkable H₂ sensitivity appears, even at room temperature. Similar situations hold in the loading of other Pd salts.

Solidification Structures in Single Crystal Copper-Rhodium Alloys with [Rh] < 15 at.%

C. TSELENTIS, M. JARDINIER-OFFERGELD and F. BOUILLON, *Ann. Chim. (Paris)*, 1984, **9**, (2), 141-144

Cu-Rh single crystal alloys containing 1.5-15 at.% Rh were grown unidirectionally from the melt. A dendritic-cellular or sometimes dendritic structure as predicted by Tittle's criteria occurred, and could be identified by microscopy after chemical etching. It is shown that this microsegregation could be reduced by high temperature annealing. Times required to homogenise the solidification structures are shorter than the values predicted by the Fleming model.

Electrical Resistance in Superconducting Amorphous Alloy Zr₇₀Ir₃₀

N. TOYOTA, A. INOUE, K. MATSUZAKI, T. FUKASE and T. MASUMOTO, *J. Phys. Soc. Jpn.*, 1984, **53**, (3), 924-927

The electrical resistance of Zr₇₀Ir₃₀ ($\rho = 300 \mu \Omega$ cm, T_c = 3.67K) was examined. The resistance increases by 3.7% on cooling from 300K down to 10K where it has a hump, and then decreases rapidly approaching T_c. Above 27K any magnetoresistance is not detected, but between 1.7K \leq T \leq 27K a positive magnetoresistance is seen and becomes saturated above H_s = 12-13T.

Surface Coordination Chemistry of Ruthenium. A Survey of Ruthenium (001) Surface Chemistry

K. L. SHANAHAN and E. L. MUETTERTIES, *J. Phys. Chem.*, 1984, **88**, (10), 1996-2003

The chemisorption behaviour of a range of organic and inorganic molecules on the basal plane of Ru, Ru(001) was studied. The close-packed Ru surface proved to be very reactive and most of the studied molecules were irreversibly chemisorbed at 25°C. Only CO, PF₃, CF₃CN, HCN and (CN)₂ showed some degree of molecular thermal desorption after adsorption at 25°C.

CHEMICAL COMPOUNDS

Synthesis of the First Pt-Au Cluster by an Unexpected H⁺-Substitution at *trans*-PtH(Cl)L₂

P. BRAUNSTEIN, H. LEHNER, D. MAT, A. TIRIPICCHIO and M. TIRIPICCHIO-CAMELLINI, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, (4), 304-305

In a novel type of exchange reaction at monohydridoplatinum complexes, *trans*-PtH(Cl)L₂ (L = phosphane), H⁺ is replaced by Au₂L₂. The compound formed is the first to contain Pt-Au bonds.

A New Type of Decaosmium Cluster Geometry: the Synthesis and X-Ray Structure Analysis of Os₁₀(S)₂(CO)₂₃

J. P. ATTARD, B. F. G. JOHNSON, J. LEWIS, J. M. MACE, M. McPARTLIN and A. SIRONI, *J. Chem. Soc., Chem. Commun.*, 1984, (9), 595-597

Pyrolysis of Os₃(CO)₁₂ with elemental S gives a range of clusters including Os₃(S)₂(CO)₉, Os₅S(CO)₁₅, Os₆(CO)₁₈, Os₇(S)₂(CO)₂₀ and Os₁₀(S)₂(CO)₂₃. X-ray analysis shows that the last cluster has a new type of Os₁₀ metal core geometry.

Synthesis of Ruthenium and Osmium Dichalcogenide Single Crystals

H. EZZAOÛIA, R. HEINDL and J. LORIERI, *J. Mater. Sci. Lett.*, 1984, 3, (7), 625-626

Single crystals of Ru and Os dichalcogenides have been grown for the first time using molten Te and, in the case of RuS₂ and OsS₂, also molten S.

Pentamethylcyclopentadienyl Diruthenium Chemistry

N. J. FORROW and S. A. R. KNOX, *J. Chem. Soc., Chem. Commun.*, 1984, (11), 679-681

The chemistry of the di-Ru centre, when stabilised by η-C₅Me₅ ligands, provides examples of new organic transformations such as isomerisation of ethylene to ethylidene and addition of ethylene to vinylidene. It also provides examples of new species such as Ru₂(CO)₂(μ-H₂)(η-C₅Me₅)₂.

ELECTROCHEMISTRY

Application of the S.P.E. Method to Organic Electrochemistry. IV. Electrochemical Reduction of Aromatic Nitro Compounds on Pt-S.P.E.

Z. OGUMI, H. YAMASHITA, K. NISHIO, Z. TAKEMARA and S. YOSHIZAWA, *Denki Kagaku*, 1984, 52, (3), 180-184

The electrochemical reduction of nitrobenzene and nitrobenzene sulphonic acid was studied on Pt-S.P.E. prepared with Nafion as the S.P.E. material. The reduction of m-nitrobenzene sulphonic acid yielded metanilic acid with very high current efficiency. No reaction selectivity was observed between the two products on Pt-S.P.E., although conditions were favourable to p-aminophenol production.

Reactions of Colloidal Platinum in Aqueous Solutions Containing Methyl Viologen, Its Cation Radical, and Hydrogen, Studied by Pulse Radiolysis

M. BRANDEIS, G. S. NAHOR and J. RABANI, *J. Phys. Chem.*, 1984, 88, (8), 1615-1623

The reactions of methyl viologen ions, MV²⁺ and MV^{•+} and H₂ in the presence of colloidal Pt were investigated by pulse radiolysis. In pH range 1.5-4 all the reducing species were converted into H₂. At pH 10, practically all the reducing species produce MV^{•+}, while from pH 6-8 the predominant species were Pt particles loaded with H₂ as hydride ions.

Hydrous Oxide Formation on Platinum - A Useful Route to Controlled Platinization

L. D. BURKE and M. B. C. ROCHE, *J. Electroanal. Chem. Interfacial Electrochem.*, 1984, 164, (2), 315-334

The formation of thick hydrous oxide films on Pt under triangular potential cycling conditions was studied as a function of sweep rate, sweep limits and pH. The results showed that increasing the cycling rate (from 5-100V/s) decreased the optimum upper limit (from 2.8-2.2V in acid) for thick film growth. Hydrous oxide growth was observed in both acid and base but not at intermediate pH values of 4.0-9.0. A brief study of the methanol electrooxidation reaction at initially smooth Pt activated by potential cycling and followed by cathodic reduction of the hydrous film, showed that excellent control of the surface roughness and, hence, the level of electrocatalytic activity of the electrode surface was possible.

Specific Features of the Adsorption of Organic Compounds on Platinum at High Positive Potentials. Methanol Solutions

L. A. MIRKIND, V. E. KAZARINOV, G. L. AL'BERTINSKII and V. N. ANDREEV, *Akad. Nauk SSSR, Elektrokhim.*, 1984, 20, (7), 883-887

Studies were made of the mechanism of adsorption of organic compounds on Pt anodes in aqueous and methanol solutions. The effect of the potentials, time of adsorption, volumetric concentration of adsorbate and potential of electroadsorption on the amount of firmly adsorbed particles and the nature of the solvent was studied. Detailed explanations are provided.

Potentials of Zero Charge and the Electric Double Layer Structure of Platinum and Palladium in Dimethylsulphoxide

E. YU. ALEKSSEVA, V. A. SAFONOV and O. A. PETRII, *Akad. Nauk SSSR, Elektrokhim.*, 1984, 20, (7), 945-950

Curves of the differential capacity were measured on renewable Pt and Pd electrodes in perchlorate solutions and alkali metal halogenides in dimethylsulphoxide (DMSO). The potentials of zero charge were found to be -0.15 and 0V for Pt and Pd, respectively. A considerable surface activity of DMSO on Pt and Pd was established together with the growth of specific adsorbed anions in the order ClO₄⁻ < Cl⁻ < Br⁻ < I⁻ and weak surface activity of cations which increased in the order Li⁺ < Na⁺ < K⁺.

Effect of Platinum Elements Additions on the Active Dissolution of Plastic Chromium in Sulfuric Acid

N. D. TOMASHOV, G. P. CHERNOVA and E. N. USTINSKY, *Corrosion (Houston)*, 1984, 40, (3), 134-137, 138

Alloys based on plastic Cr with 0.1-0.4wt.% Ru, Pt, Ir or Pd were investigated in 40% H₂SO₄ in the active state under cathodic polarisation (-0.175V). All the studied additions of delaying elements are responsible for the reduced anodic dissolution of Cr. Two mechanisms decelerated the dissolution.

Hydrogen Chemical Potentials, Surface Heterogeneities and Solution Diffusive Processes in Hydrogen Electrode Reactions

F. A. LEWIS, R. C. JOHNSTON, S. G. McKEE, A. OBERMANN and M. C. WITHERSPOON, *Int. J. Hydrogen Energy*, 1984, **9**, (4), 303-307

Surface and substrate H potential measurements were used to find rates of permeation of dissolved H₂ molecules to and from Pd and Pd alloy electrode surfaces through the Brunner-Nernst layer. These co-joint measurements made it possible to compare the upper limiting H chemical potentials at catalytically active surfaces under H bubble evolution during electrolysis in acid, alkaline and neutral salt solutions. (57 Refs.)

Hydrolysis of the Palladium(II) Ion in a Sodium Chloride Medium

N. B. MILIC and Z. D. BUGARCIC, *Transition Met. Chem.*, 1984, **9**, (5), 173-176

The hydrolysis of the Pd(II) ion in a NaCl medium was studied at 25°C by the e.m.f. method. The extent of the Pd hydrolysis depends upon the concentration of both Pd and the NaCl medium. Thus the extent of hydrolysis increases with increasing Pd concentration at a definite pH, but decreases with increasing NaCl concentration. The stability constants of the complexes obtained, PdOH⁺ and Pd₄(OH)₄⁴⁺ also differ slightly, depending upon the NaCl concentration.

Dioxygen Evolution from Inorganic Systems. Water Oxidation Mediated by RuO₂ and TiO₂-RuO₂ Colloids

C. MINERO, E. CORENZI, E. PRAMAURO and E. PELIZZETTI, *Inorg. Chim. Acta Articles and Letters*, 1984, **91** (b9), (4), 301-305

The kinetics of reduction of aqueous solutions of Ce^{IV} and Ru(bpy)₃³⁺ in the presence of catalytic amounts of RuO₂ colloids stabilised with polybrene and colloidal TiO₂ particles loaded with RuO₂ have been investigated by stopped-flow spectrophotometric techniques. The effect of pH, catalyst preparation and loading concentration have been considered. The TiO₂/RuO₂ colloidal particles (45nm radii) are extremely active catalysts.

Studies of the Stability of RuS₂ Single Crystals and the Photo-Oxidation of Halides

H. EZZOUJA, R. HEINDL, R. PARSONS and H. TRIBUTSCH, *J. Electroanal. Chem. Interfacial Electrochem.*, 1984, **165**, (1/2), 155-166

Anodic photocorrosion of n-RuS₂ is very slow under moderate conditions but can be accelerated under extreme conditions of high potentials and rapid O₂ evolution. The stability is mainly thermodynamic, but may be kinetic to some extent. RuS₂ shows an onset of photocurrent which is shifted strongly to lower potentials in the series Cl⁻, Br⁻, I⁻. This is related to improved kinetics of the oxidation reaction due to adsorption of the intermediate species.

PHOTOCONVERSION

Visible Light Induced Hydrogen Production from in Situ Generated Colloidal Rhodium-Coated Cadmium Sulfide in Surfactant Vesicles

Y.-M. TRICOT and J. H. FENDLER, *J. Am. Chem. Soc.*, 1984, **106**, (8), 2475-2476

The first use of vesicle-stabilised, in situ formed, Rh catalyst-coated colloidal semiconductor CdS in artificial photosynthesis is reported. Band-gap excitation by visible light ($\lambda > 350\text{nm}$) of Rh-coated CdS in dihexadecylphosphate surfactant vesicles produced H₂ in the presence of thiophenol, and the H₂ production was sustained for approximately 48h. After 48h, more than 90% of PhSH was consumed. These systems may provide means for viable solar energy conversion.

Photochemistry of the Tris(2,2'-bipyridine) Ruthenium(II) - Peroxydisulfate System in Aqueous and Mixed Acetonitrile-Water Solutions. Evidence for a Long-Lived Photoexcited Ion Pair

H. S. WHITE, W. G. BECKER and A. J. BARD, *J. Phys. Chem.*, 1984, **88**, (9), 1840-1846

The photooxidation of Ru(bpy)₃²⁺ by peroxydisulphate, was investigated by steady-state luminescence quenching and emission lifetime techniques in aqueous and mixed CH₃CN-H₂O solutions. The results are consistent with the formation of a ground-state ion pair [Ru(bpy)₃²⁺.S₂O₈²⁻]. The lifetime of the photoexcited ion pair-ion pair association constant and oxidative rate constant are reported for aqueous and CH₃CN-H₂O solutions. The lifetime of the photoexcited ion pair [Ru(bpy)₃²⁺.S₂O₈²⁻]* is unusually long, ranging from 0-11 μs in H₂O to 0-53 μs in 50% CH₃CN.

Photosubstitution Reactions of Ru(bpy)₂XYⁿ⁺ Complexes

D. V. PINNICK and B. DURHAM, *Inorg. Chem.* 1984, **23**, (10), 1440-1445

The quantum yields for the photosubstitution of a series of Ru(bpy)₂XYⁿ⁺ complexes have been measured. The ligands X and Y span the range of the spectrochemical series from Cl⁻ to CO. The correlation between the energy of the lowest energy charge-transfer transition and quantum yield is discussed.

Improvement of the Photoelectrochemical Change of H₂S over CdS Suspensions Using RuS₂ as a Catalyst

D. H. M. W. THEWISSEN, E. A. VAN DER ZOUWEN-ASSINK, K. TIMMER, A. H. A. TINNEMANS and A. MACKOR, *J. Chem. Soc., Chem. Commun.*, 1984, (14), 941-942

Illumination of a suspension of CdS particles loaded with 0.5wt.% RuS₂ leads to photocatalytic H₂ evolution from alkaline S²⁻/SO₃²⁻ solutions with a formal quantum efficiency of 0.12 at 470nm; in comparison with the analogous system, CdS/0.5wt.% RuO₂, this represents an improvement by a factor of 7.

LABORATORY APPARATUS AND TECHNIQUE

A Miniature Palladium-Palladium Oxide Enzyme Electrode for Urea Determination

N. J. SZUMINSKY, A. K. CHEN and C. C. LIU, *Biotechnol. Bioeng.*, 1984, **26**, (6), 642-645

The preparation and evaluation of Pd-PdO pH urea electrodes, based on the combination of immobilising urease are described. Full response of the urea electrode was obtained five minutes after transferring the electrode into the test buffer solution, the response characteristics were sensitive to details in the urease-BSA coating of the Pd-PdO pH electrode, and gave reproducible results. The electrode was stable for more than three weeks when EDTA was added to the test and storage buffer solutions.

Magnetic Compton Profile Measurement Using Circularly Polarized Gamma-Rays from Oriented ^{191m}Ir Nuclei

N. SAKAI, O. TERASHIMA and H. SEKIZAWA, *Nucl. Instrum. Methods Phys. Res.*, 1984, **221**, (2), 419-426

Circularly polarised 129keV γ -rays from oriented ^{191m}Ir nuclei were used to measure the Compton profile of magnetic electrons in ferromagnetic Fe. Radioactive isotope ^{191}Os (which decays to ^{191}Ir) in Fe metal, $^3\text{He}/^4\text{He}$ dilution refrigeration and a solid state detector with a large active diameter remarkably improved the accuracy of the magnetic Compton profile measurement.

HETEROGENEOUS CATALYSIS

Kinetics of Hydrogenation of Melted Benzoic Acid on Palladium Catalyst

V. YU. KONYUKHOV, I. M. GENKINA, D. I. PERAZICH, N. V. KULKOVA and M. I. TEMKIN, *Akad. Nauk SSSR, Kinet. Katal.*, 1984, **25**, (3), 578-582

The rate of hydrogenation of melted benzoic acid was measured on suspended Pd/activated C catalyst at 130, 150 and 170°C and H_2 pressure of 0.8-5MPa. An agreement was observed between the kinetic equation previously established and the present measurement. The kinetic equation could be applied to hydrogenation processes of benzoic acid.

Hydrogenolysis of Alkanes. Part I. - Hydrogenolysis of Ethane, Propane and n-Butane on 6% Pt/SiO₂ (EUROPT-1)

G. C. BOND and X. YIDE, *J. Chem. Soc., Faraday Trans. 1.*, 1984, **80**, (4), 969-980

The hydrogenolysis of ethane, propane and n-butane was studied on a 6.3%Pt/SiO₂ catalyst (EUROPT-1). Treatment of the catalyst in H_2 at 623-1173K led to a loss of capacity for H_2 chemisorption greater than that attributable to an increase in particle size and to an even greater loss of activity of n-butane hydrogenolysis, which was partly restorable by oxidation. Extensive reorganisation of the metal occurs during a short oxidation at 873K.

Catalysis of the Exchange of Hydrogen and Carbon Isotopes in the Water/Hydrogen and Bicarbonate/Formate Redox Couples: A Comparison of the Exchange Current Densities on Palladium

S. CHAO, C. J. STALDER, D. P. SUMMERS and M. S. WRIGHTON, *J. Am. Chem. Soc.*, 1984, **106**, (9), 2723-2725

The exchange of H and C isotopes in the $\text{CO}_3\text{H}^-/\text{HCO}_2^-$ aqueous redox couple occurs at a rate that is of the same order of magnitude as the H isotope exchange in the $\text{H}_2\text{O}/\text{H}_2$ aqueous redox system at 298K, using a Pd based heterogeneous catalyst. The catalysts were Pd, Pt on C, PQ.

A Study of the Structure Sensitivity of the Propylene Hydrogenation Reaction over Supported Platinum and Palladium Catalysts

E. RORRIS, Ph.D.Thesis, Northwestern Univ., 1983, *Diss. Abstr. Int. B*, 1984, **44**, (10), 3146

Propylene hydrogenation was investigated over a series of Pt/SiO₂ and Pd/SiO₂ catalysts; preparations, pretreatments and morphologies were examined. On Pt/SiO₂ prepared by impregnation a four-fold enhancement in the turnover frequency occurred as the temperature of treatment in H_2 decreased 450°C to -50°C. Pd/SiO₂ had a maxima in the turnover frequency at a H_2 treatment temperature of ~100°C. Formation of β -phase of Pd hydride reduced the catalytic activity. Pd catalysts were much more active than Pt catalysts in hydrogenating propylene.

The Oxidation of CO and Hydrocarbons over Noble Metal Catalysts

Y.-F. YU YAO, *J. Catal.*, 1984, **87**, (1), 152-162

The oxidation of CO, C₃H₆, 1-hexene and toluene under excess O₂ was studied over Pt, Pd and Rh in the form of unsupported wires or supported on γ -Al₂O₃ or CeO₂/Al₂O₃. The kinetics were affected by the state of metal dispersion, pretreatment temperature, reaction conditions and the presence of CeO₂. Two types of surface sites are postulated to explain the results.

Effects of Catalyst Addition to Coal on CO₂ Adsorption Kinetics of Coal and Char

K. OTTO, H. SOREK, L. BARTOSIEWICZ and M. SHELEF, *Fuel*, 1984, **63**, (4), 477-481

The surface area of Illinois No. 6 coal, impregnated with a series of C gasified catalysts, including Ru, Pd, Pt and Rh was measured by CO₂ adsorption before and after pyrolysis. Catalyst addition decreased the surface area of coal accessible to CO₂ in all cases.

Catalytic Combustion

R. PRASAD, L. A. KENNEDY and E. RUCKENSTEIN, *Catal. Rev. - Sci. Eng.*, 1984, **26**, (1), 1-58

A review is given of principles of catalytic combustion, NO_x formation and control, catalyst systems including Pt, Ru, Pd, Os and Ir catalysts, and the kinetics of fuel oxidation. (127 Refs.)

Mechanism of Reactions on Multimetallic Catalysts

L. GUCZI, *J. Mol. Catal.*, 1984, **25**, 13-29

A review is given of the mechanism of hydrocarbon reactions carried out on supported and unsupported Ru-Cu, Ru-Au, Ru-Pt, Ru-Fe, Pt-Au, Pt-Ir, Pt-Fe bimetallic systems, by considering the effect of particle size, dispersion, matrix effect, change in H₂ coverage, metal-support interaction and suppression of ageing effects. (98 Refs.)

Preparation of Catalysts. Part 2. Depositing a Metal Compound on a Support. Impregnation and Drying

C. MARCILLY and J.-P. FRANCK, *Rev. Inst. Fr. Pet.*, 1984, **39**, (3), 337-364

Impregnation and drying, which are two of the operating principles involved in preparing supported metal catalysts are examined. An analysis of the different phenomena accompanying the drying of a simple system composed of one or two pores, then of a more complex system made up of a support with a wide pore distribution, is given. Among complexes examined are IrCl₃³⁻, PdCl₄²⁻ and Pt(NH₃)₄²⁺ (56 Refs.)

Synthesis Gas Conversion Utilizing Mixed Catalyst Composed of CO Reducing Catalyst and Solid Acid. II. Direct Synthesis of Aromatic Hydrocarbons from Synthesis Gas

K. FUJIMOTO, Y. KUDO and H.-O. TOMINAGA, *J. Catal.*, 1984, **87**, (1), 136-143

The synthesis of aromatic hydrocarbons from CO and H₂ was studied under pressure using Pd/SiO₂ and zeolites. Combination of Pd/SiO₂ with H-ZSM-5 or H-mordenite gave aromatic hydrocarbons with selectivities > 50%. Pd/SiO₂ with H-Y gave few aromatics. Tetramethyl and pentamethyl benzenes were mostly formed on H-ZSM-5, significantly different from aromatics formed by the methanol reaction on H-ZSM-5.

Optimize Syngas to Naphtha over Ruthenium Catalysts

R. A. STOWE and C. B. MURCHISON, *Hydrocarbon Process.*, 1984, **63**, (6), 95-100

The optimisation of a catalyst system for production of crackable feedstock from the partial combustion cracking byproduct syngas was investigated. A series of studies with a number of Co and Ru catalysts using various supports, such as C, Al₂O₃, H-ZSM-5 zeolite, silica gel and silicalite were performed. Studies were also done with K-promoted Ru/Al₂O₃ catalysts and Ru-Ni/Al₂O₃ catalysts. Results were compared, selectivities examined and the effects of surface area were measured. The H₂:CO ratio was fixed by the conditions of the ethylene production process, and to maximise the C₂₊ selectivity to obtain the highest possible yield of feedstock crackers to ethylene. An optimised K-promoted Ru/Al₂O₃ catalyst had campaigns of over 1000 hours on stream. The C₂₊ selectivities averaged ~90%.

Promoting Effect of V, Mo, W and Re on the Rate of C-O Bond Dissociation of Adsorbed CO in Methanation on Ru/Al₂O₃

T. MORI, A. MIYAMOTO, N. TAKAHASHI, M. FUKAGAYA, H. NIIZUMA, T. HATTORI and Y. MURAKAMI, *J. Chem. Soc., Chem. Commun.*, 1984, (11), 678-679

Studies of the effect of the addition of V, Mo, W and Re on the rate of C-O bond dissociation of adsorbed CO in methanation on Ru/Al₂O₃ catalysts was made using pulse surface reaction rate analysis, coupled with an emissionless diffuse reflectance i.r. spectrometer. The addition of these elements was found to increase greatly the rate of dissociation.

High Molecular Weight Hydrocarbons from the Fischer-Tropsch Process with a Pre-oxidized Ruthenium Zeolite Catalyst

M. AUDIER, J. KLINOWSKI and R. E. BENFIELD, *J. Chem. Soc., Chem. Commun.*, 1984, (9), 626-628

The catalytic performance of zeolite based Ru catalyst in the Fischer-Tropsch reaction depends on the sequence of oxidation/reductions to which they are subjected. With finely divided Ru particles, obtained by reducing [Ru(NH₃)₆]³⁺-exchanged synthetic faujasitic zeolite, CH₄ is the main product, but when the zeolite is first oxidised in air at 400°C, forming RuO₂ crystallites which can then be reduced, longer-chain hydrocarbons are produced at low reaction temperatures (155°C).

HOMOGENEOUS CATALYSIS

Gas Phase Acetoxylation of 1,3-Butadiene over Palladium Catalysts. Part 1. The Catalytic Activity and Structure of Pd-Sb-KOAc Catalysts

H. SHINOHARA, *Appl. Catal.*, 1984, **10**, (1), 27-42

The gas phase acetoxylation of 1,3-butadiene over Pd catalysts was studied. The Pd-KOAc catalyst gave a very low activity and selectivity to 1,4-diacetoxybutene-2. The main product was 1-acetoxy-1,3-butadiene but, by adding some third components to the catalyst, higher activity and selectivity were obtained; Sb and Bi were the most effective third components. The highest activity was obtained at ~0.4 Sb:Pd atomic ratio. It is concluded that the active species on the Pd-Sb-KOAc catalyst is an intermetallic compound, such as Pd₃Sb.

Comparison of Homogeneous and Heterogeneous Palladium Hydrogenation Catalysts

J. A. HELDAL and E. N. FRANICEL, *J. Am. Oil Chem. Soc.*, 1984, **61**, (4), 756-761

Mechanistic and kinetic studies of Pd-catalysed hydrogenation at atmospheric pressure and 30-100°C were carried out with methyl sorbate, methyl linoleate and conjugated linoleate. Homogeneous Pd catalysts and particularly Pd-acetylacetonate [Pd(acac)₂] were significantly more selective than Pd/C in the hydrogenation of sorbate to hexenoates, mainly trans-2-hexenoate.

Synthetic Applications of the Palladium-Catalyzed Oxidation of Olefins to Ketones

J. TSUJI, *Synthesis*, 1984, (5), 369-384

A review of the oxidation of olefins to ketones with Pd(II) salts is presented. Emphasis is placed on the catalytic oxidation of terminal olefins to methyl ketones and the application to organic synthesis. Also regioselective oxidation of some internal olefins by the participation of O functions is given. (120 Refs.)

Oxo Complexes of Ruthenium (VI) and (VII) as Organic Oxidants

G. GREEN, W. P. GRIFFITH, D. M. HOLLINGSHEAD, S. V. LEY and M. SCHRÖDER, *J. Chem. Soc., Perkin Trans. I*, 1984, (4), 681-686

Oxidation of a variety of saturated and unsaturated primary and secondary alcohols by $[\text{RuO}_4]^{2-}$, $[\text{RuO}_4]^-$, trans-Ba $[\text{Ru}(\text{OH})_2\text{O}_3]$, $[\text{RuO}_2\text{Cl}_3]^-$ and $[\text{RuO}_2(\text{bipy})\text{Cl}_2]$ was studied. $[\text{RuO}_4]^{2-}$ was found to be useful catalytically in conjunction with $[\text{S}_2\text{O}_8]^{2-}$ under basic aqueous conditions. Both $[\text{RuO}_4]^{2-}$ and $[\text{RuO}_4]^-$ oxidise primary alcohols to carboxylic acids and secondary alcohols to ketones. The new species $[\text{PPh}_4][\text{RuO}_2\text{Cl}_3]$ and also $[\text{RuO}_2(\text{bipy})\text{Cl}_2]$ cleanly oxidised a wide range of alcohols to aldehydes and ketones without attacking double bonds.

CORROSION PROTECTION

Detection of Hydrogen Generated by Corrosion Reactions Using a Solid Electrolyte Probe

S. B. LYON and D. J. FRAY, *Mater. Perform.*, 1984, 23, (4), 23-25

A solid state electrolyte probe for H_2 detection either inside solid steel pipes or in the environment has been developed. The probe has different designs depending on the application but all use Pd. The probes are used to monitor corrosion in steel.

ELECTRICAL AND ELECTRONIC ENGINEERING

Thermoelectric Effects in Cold Work in Pt/10%Rh and Pt/13%Rh Versus Pt Thermocouples

R. E. BENTLEY and T. L. MORGAN, *Metrologia*, 1984, 20, (2), 61-66

The effects of cold work introduced in handling Pt-Rh:Pt thermocouples have been investigated. Changes in the Seebeck coefficient of up to $-40\text{mV}/^\circ\text{C}$ and errors in calibration of up to -0.4% were found. Above 200°C recovery in the Seebeck coefficient toward its pre-cold-worked value occurred at an increasing rate with temperature, but in the Pt-Rh leg, unlike the Pt leg, the recovery was incomplete. A residual effect, attributed to Pt-Rh, of up to $-4\mu\text{V}$ remained in the thermocouple e.m.f. after recovery anneals had been applied. Recommendations are made for handling high quality Pt-based thermocouples.

The Effect of Environment and Materials Properties on the Friction and Wear Behaviour of Precious Metal Electrical Contact Alloy Couples

L. E. POPE and R. W. ROHDE, *IEEE Trans. Components, Hybrids, Manuf. Technol.*, 1984, CHMT-7, (1), 56-60

The friction and wear behaviour of Pd base (ASTM B540) alloy couple and Au base (ASTM B541) were tested in air with 35-45% relative humidity, high purity air and in ultra high purity He. The microstructures and hardness were varied by age hardening, heat treatments and/or cold rolling. The poorest friction performance occurred in the He atmosphere. O_2 in the environment improved the unlubricated friction performance significantly.

High-Efficiency Ion-Implanted Silicon Solar Cells

M. B. SPITZER, S. P. TOBIN and C. J. KEAVNEY, *IEEE Trans. Electron Devices*, 1984, ED-31, (5), 546-550

The development of solar cells with AM1 conversion efficiency of 18% is reported. The cell comprises an $n^+p\text{-}p^+$ structure, fabricated from float zone Si of resistivity $0.3\Omega\text{cm}$. The front contact pattern made for Ti-Pd-Ag yielded a shadow loss of 3-4%. The back contact was formed by full-area Ti-Pd-Ag metallisation. The growth of SiO_2 passivation for reduction of the surface recombination velocity was shown to be important for high cell performance.

Properties of Galvanic Pd-Ni-Coatings at Plug Contact

H. GROSSMAN, M. HUCK and G. SCHAUDT, *Metall (Berlin)*, 1984, 38, (7), 631-639

The properties of PdNiX (X=20,35) electrodeposits (with and without AuCo flash) are discussed in comparison to AuCo and Pd+Au-Co(fl). SEM and optical investigations, and measurements of microhardness, frictional forces, contact resistance and internal stress of the electrodeposits were used to describe the friction wear characteristics. The electrodeposits were corroded in H_2S , SO_2 and NO_2 at 400 ppb each for 6 days, and after exposure at 398K and 473K for 96 hours. The PdNi20+AuCo(fl) layers on connectors were found to be at least equivalent to high carat AuCo and Pd+AuCo(fl). The Pd and Ni were in solid solution.

Measurement of the Tunnelling and Hopping Parameters in RuO_2 Thick Films

N. C. HALDER and R. J. SNYDER, *Electrocomponent Sci. Technol.*, 1984, 11, (2), 123-136

Thick film resistors containing a mixture of conductive RuO_2 and $\text{Pb}_5\text{B}_2\text{SiO}_{10}$ have been produced on $[(\text{Al}_2\text{O}_3)_{0.96}(\text{MgO})_{0.04}]$ substrates. The TCR of the films was measured for different particle size and concentration of the conductor particles. The TCR was a function of temperature in all the films. From the measured values of negative TCR the tunnelling parameter α and hopping parameter β were determined. The results suggest that hopping is important for the low concentration films.